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Structure, Chemical Properties and Thermal Decomposition of Cadmium Methoxide and Cadmium Ethoxide*

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The structure of both cadmium methoxide and cadmium ethoxide is of a partially ordered random-layer type. X-ray diffraction patterns can be interpreted in terms of hexagonal crystal lattice with unit-cell parameters: $a = 3.494(3)$, $c = 8.36(1)$ Å for cadmium methoxide, $a = 3.482(3)$, $c = 8.98(1)$ Å for cadmium ethoxide. Powder diffractometer data for both compounds and IR spectrum for cadmium ethoxide are given.

The stability of the compounds was checked at room temperature in air. Thermal decomposition was investigated by DTA and X-ray diffraction. The decomposition of cadmium ethoxide results in the formation of CdO, while the elemental Cd and, to a much smaller extent, CdO are products of the decomposition of cadmium methoxide. The decomposition of cadmium methoxide and ethoxide was also studied by mass spectrometry. The mechanism of decomposition is discussed. The intermediate formation of carbene, $:CH_2$, is suggested in decomposition of cadmium methoxide.

INTRODUCTION

Very few papers on cadmium alcoxides have been published by now. Turevskaya, Turova and Novoselova[1] studied the conditions of synthesis and the properties of the methoxides and ethoxides of Zn, Cd and Hg. It was found that the exchange reactions of the corresponding anhydrous acetates

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with sodium methoxide or ethoxide or with lithium ethoxide in alcohol medium lead to the formation of alcoxides practically free of impurities. Turova and Turevskaya[2] published the results of X-ray diffraction and IR spectroscopy investigations of zinc, cadmium and mercury methoxides and cadmium and mercury ethoxides.

Nakasugi, Ishimori and Tsuruta[3] studied the affinity of $CdEt_2$ toward Lewis oxygen and sulfur bases by infrared frequency shifts of $CdEt_2$. Linear relationships were observed for the plots of frequency shifts $\Delta\nu_a$ (C—Cd—C) of $CdEt_2$ vs. $\Delta\nu_a$ (C—Zn—C) of $ZnEt_2$ and $\Delta\nu_a$ (C—Cd—C) of $CdEt_2$ vs. $\Delta\nu$ (O—D) of CH_3OD. The reliability of the results for $CdEt_2$ was roughly checked for the spectra of reaction products between $CdEt_2$ and CH_3OH.

Therefore, it should be pointed out that cadmium alcoxides are almost unknown compounds of appreciable scientific interest.

In the present paper, a modified procedure in the preparation of cadmium methoxide and ethoxide was applied. Crystal structure, stability and thermal decomposition were studied using different experimental methods: X-ray diffraction, DTA, IR spectroscopy, mass spectrometry, scanning electron microscopy.

EXPERIMENTAL

Following the basic ideas given by Turevskaya *et al.*[1] an elegant procedure of cadmium methoxide and ethoxide preparation was developed. The procedure is based on the exchange reaction of anhydrous cadmium acetate with sodium methoxide or ethoxide in methanol or ethanol, respectively.

$Cd(OAc)_2 \cdot 2H_2O$ was dehydrated in a weighing bottle (filled to about one third of its height) in a vacuum furnace at 406—408 K (133—135 °C). The increase of temperature was very slow (4 hours). During the first two hours the pressure was low (17—34 kPa) and then increased to above 100 kPa. Anhydrous cadmium acetate was obtained after 10 hours under these conditions.

Approx. 1 g Na was added to 200 ml absolute, freshly distilled MeOH or EtOH at 293 K (20 °C). The solution was stirred until all metallic sodium was dissolved. A solution of about 2.2 g $Cd(OAc)_2$ in 100 ml freshly distilled absolute MeOH or EtOH was added slowly (dropwise) at 323—343 K (50—70 °C) into the solution of sodium methoxide or ethoxide, respectively, previously heated to boiling $\sim$ 353 K ($\sim$ 80 °C) in a 500 ml round bottom flask with reflux condenser equipped with a drying inverted tube. The reaction mixture was stirred rapidly as addition took place. Colloidal particles of cadmium methoxide (ethoxide), formed during addition of cadmium acetate solution, were precipitated overnight. Supernatant was removed by pipet, 250 ml of fresh methanol (ethanol) was added and the suspension boiled for 3 hrs. This operation was repeated, alcohol was removed, and the residue was filtered in a glove box (in the presence of P_2O_5), washed with methanol (ethanol) and dried in vacuum desiccator.

The yields of cadmium methoxide and ethoxide syntheses were 80.2 to 88.3% (mean value of 5 preparations: 83.6%) and 65.1 to 78.9% (mean value of 3 preparations: 72.0%) respectively. The literature yields[1] are 95 and 70%, respectively.

The crystal structure of cadmium methoxide and ethoxide was determined by X-ray diffraction. Their stability and thermal decomposition were investigated by mass spectrometry, differential thermal analysis, and X-ray diffraction. Cadmium ethoxide was also studied by IR spectroscopy (4000—400 cm^{-1}). Optical and electron scanning microscopy were used to study the particle shape.

RESULTS AND DISCUSSION

Cadmium methoxide and ethoxide, prepared by the procedure described in the previous section, are white polycrystalline solids (see SEM of cadmium methoxide sample, Figure 1), insoluble in abs. alcohol, acetone, acetylacetone, benzene, carbon tetrachloride, chloroform, cyclohexane, dichloromethane, ethy-

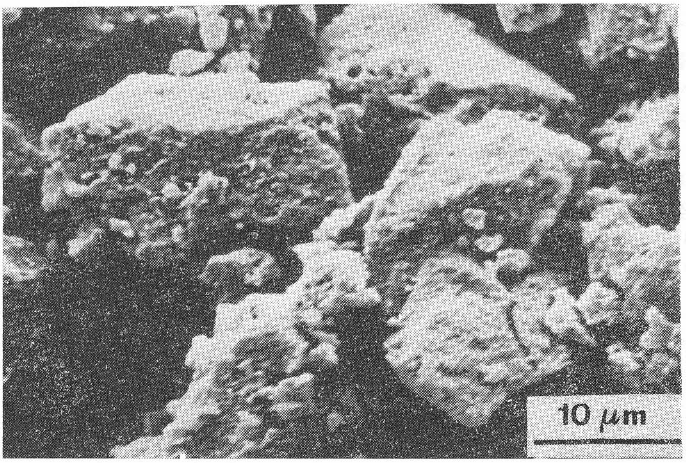


Figure 1. Scanning electron micrographs of cadmium methoxide sample.

lene glycol, dimethylether, bis(2-ethoxyethyl)ether, dimethylformamide, dimethyl sulfoxide, pyridine, and tetrahydrofuran.

TABLE I

Infrared Frequencies (cm^{-1}) of Freshly Prepared $Cd(OEt)_2$

Wave numbers of absorption bands				Assignement of frequencies	
Nujol NaCl cell ◆	This work CCl_4 NaCl cell ▼	KBr pressed pellet ●	Literature Ref. 2	This work	Literature Ref. 2
3660 (m)	3659 (s)	3647 (s)	—	?	
—	2941 (vs)	2940 (vs)	2949 (vs)	ν (C—H)	$^{\nu}$C—H, $^{2\delta}$C—H
—	2905 (s)	2908 (s)	2911 (s)	↓	The same
—	2836 (s)	2840 (s)	2841 (s)	Overtones	,,
—	2813 (s)	2810 (s)	2813 (m)	and combi-	,,
—	—	—	2773 (w)	nations	,,
2679 (m)	2679 (m)	2684 (m)	—		
2593 (w)	2580 (w)	2584 (w)	—		
—	2489 (w)	2489 (w)	—		
1919 (w)	1916 (w)	1919 (w)	—		
—	1720 (m)	1737 (m)	—		
1644 (w)	1640 (m)	1610 (m)	—		
—	1443 (s)	1433 (?)	1436 (m)	δ (C—H)	$^{\delta}$C—H
—	1366 (vs)	1372 (?)	1372 (vs)	,,	The same
—	1346 (s)	—	1352 (vs)	,,	,,
1103 (vs)	1101 (vs)	1092 (vs)	1104 (vs)	ν_a (C—O)	$^{\nu}$C—O
1053 (vs)	1052 (vs)	1046 (vs)	1055 (vs)	ν_s (C—O)	The same
—	—	—	980 (w)		
875 (s)	875 (s)	870 (s)	875 (s)	ν (C—C)	$^{\nu}$C—C
—	—	—	550 (sh)		$^{\nu}$M—O
—	—	512 (s)	516—490 (s)	ν_a (Cd—O)	The same
—	—	475 (m)	470 (sh)	ν_s (Cd—O)	,,

◆ mean value of 3—4 measurements, ▼ 1 measurement, ● mean value of 8—18 measurements;
vs = very strong, s = strong, m = medium, w = weak, sh = sharp

A Study of Cd(OEt)$_2$ by IR Spectroscopy

The IR spectra of freshly precipitated cadmium ethoxide were obtained by using Nujol or carbon tetrachloride (as solvents) and a sodium chloride cell. Pressed pellets with KBr were also prepared (by careful mixing of Cd ethoxide and KBr of infrared quality). The approximate volume ratio of Cd(OEt)$_2$ and KBr was 1 : 5. All IR samples were prepared in a glove box with nitrogen atmosphere and in the presence of P_2O_5. Perkin-Elmer IR-Spectrophotometer 283 was used. The results are presented in Table I and compared with the literature data.

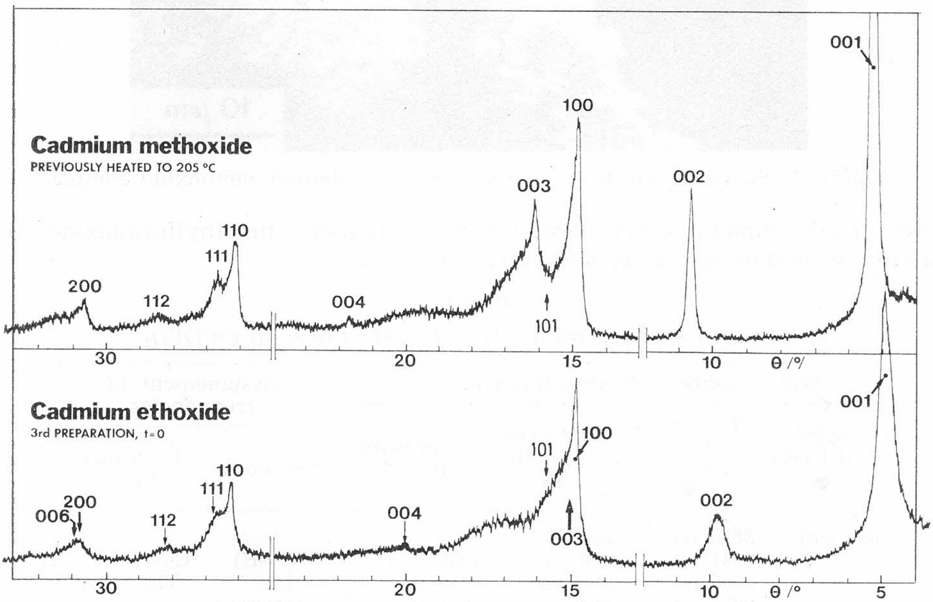


Figure 2. X-ray diffraction patterns of cadmium methoxide (previously heated to 478 K, i. e. 205 °C) and cadmium ethoxide (frechly prepared); radiation: monochromatized Cu*K*α.

TABLE II

Unit-cell Parameters and X-ray Densities of Cd (OMe)$_2$ and Cd (OEt)$_2$

	$\frac{a}{Å}$	$\frac{c}{Å}$	$\frac{c}{a}$	$\frac{\varrho_{X-ray}}{g\ cm^{-3}}$	$\frac{V = \frac{\sqrt{3}}{2} a^2 c}{Å^3}$
Cd (OMe)$_2$	3.494(3)	8.36(1)	2.39	3.277	88.39
Cd (OEt)$_2$	3.482(3)	8.98(1)	2.58	3.566	94.29

(Numbers in parentheses represent the standard deviation of the least significant digit.)

The Crystal Structure of Cadmium Methoxide and Ethoxide

The samples were studied by X-ray diffraction (at room temperature) using a counter diffractometer with monochromatized Cu$K\alpha$ radiation. X-ray diffraction patterns of cadmium methoxide and ethoxide, Figure 2, can be interpreted in terms of hexagonal crystal lattice with unit-cell parameters (determined by using an internal standard) and X-ray densities given in Table II.

The data given by Turova and Turevskaya[2], $a = 3.49(2)$, $c = 8.42(2)$ Å for Cd methoxide, $a = 3.49(1)$, $c = 9.1(5)$ Å for Cd ethoxide, are in fair agreement with ours. One can notice a great scattering of the c-parameter values for Cd ethoxide in their work. The same authors stated that the space group is $P\bar{3}m1$, with one molecule ($Z = 1$) in the unit cell.

The powder diffractometer data for $Cd(OMe)_2$ and $Cd(OEt)_2$ are given in Tables III and IV, respectively. Diffraction patterns of $Cd(OMe)_2$ and $Cd(OEt)_2$ are typical examples of a partially ordered random-layer structure, for which modulation of the two-dimensional diffraction bands is just visible. The crystallites of a substance having the random-layer structure consist of mutually parallel and equidistant layers, with regular two-dimensional lattice. The layers are stacked at random with respect to each other, i. e. the neighboring layers are mutually disoriented. Let the c axis be normal to and axes a and b parallel to the layers. The diffraction pattern of such a substance consists of symmetric crystalline lines of the type *00l* and asymmetric two-dimensional lines *hk*. The intensity of such a band falls off abruptly on the low-angle side, but gradually on the high-angle side. No general *hkl* diffraction lines are present. If here and there within the crystallites the neighboring layers are mutually in the ordered (regular) orientation, modulation of bands *hk* takes place: with the advance of ordering the bands start to split into three-dimensional diffraction lines *hk0* and *hkl*. In the case of $Cd(OMe)_2$ and $Cd(OEt)_2$ this effect is manifested as follows: band 10 appears as line 100, having line 101 as a hump on its high-angle side; band 11 occurs as line 110, with line 111 as a (weak) local maximum emerged from its high-angle side, and line 112 as a separate (weak) maximum (etc.) (Figure 2).

In contrast with the above conclusions, Turova and Turevskaya[2], mistakenly, stated that lines *00l* were blurred on the high-angle side. The theory of diffraction in the random-layer structure predicts symmetric crystalline lines *00l* and asymmetric *hk* bands. In the case of $Cd(OMe)_2$ and $Cd(OEt)_2$ lines *00l* are symmetrically broadened indicating small crystallite size in the c-direction, i. e. small thickness of the stack of layers. Lines *hk0* show a degree of asymmetry although a partial ordering of the layers takes place.

In order to define the degree of ordering of the layers Turova and Turevskaya[2] suggested the ratio of the experimental and X-ray densities. The justification of this parameter, which should mean the fraction of the ordered (regularly oriented) layers within the crystallites, can obviously be severely questioned. The fraction of the regularly oriented layers in our samples of $Cd(OMe)_2$ and $Cd(OEt)_2$ is probably small. If this fraction were much higher, one could apply parameters similar to those for graphite, which are measured from the profiles and positions of diffraction lines *hkl* and *00l*, as proposed by Franklin[4], Bacon[5] and Warren[6].

TABLE III

Powder Diffractometer Data for Cd(OMe)₂ at 298 K (Radiation: Monochromatized CuKα)

$2\,\Theta_{obs}/°$	I/I_o	d_{obs}/Å	d_{calc}/Å	h k l
10.60	10	8.35	8.36	0 0 1
21.25	2	4.18	4.18	0 0 2
29.53	3	3.025	3.026	1 0 0
32.15	1	2.785	2.787	0 0 3
43.30	$\leqslant 1$	2.090	2.090	0 0 4
52.45	1	1.745	1.747	1 1 0
53.60	<1	1.710	1.710	1 1 1
56.85	$\leqslant 1$	1.620	1.612	1 1 2
61.28	<1	1.513	1.513	2 0 0
67.20	$\leqslant 1$	1.393	1.393	0 0 6
84.68	<1	1.145	1.144	2 1 0
99.50	$\leqslant 1$	1.010	1.009	3 0 0

TABLE IV

Powder Diffractometer Data for Cd(OEt)₂ at 298 K (Radiation: Monochromatized CuKα)

$2\,\Theta_{obs}/°$	I/I_o	d_{obs}/Å	d_{calc}/Å	h k l
9.85	10	8.98	8.98	0 0 1
19.75	2	4.49	4.49	0 0 2
29.65	5	3.015	3.015	1 0 0
			2.993	0 0 3⁺
40.05	$\leqslant 1$	2.25	2.245	0 0 4
52.60	2	1.740	1.741	1 1 0
53.60	<1	1.71	1.709	1 1 1
56.45	<1	1.630	1.623	1 1 2
61.65	1	1.505	1.508	2 0 0
			1.500	0 0 6
85.10	<1	1.140	1.140	2 1 0
100.18	$\leqslant 1$	1.005	1.005	3 0 0

⁺ Line 003 overlaps with the much stronger line 1 0 0.

Thermal Decomposition of Cadmium Methoxide and Ethoxide

1. Mass Spectrometry Study

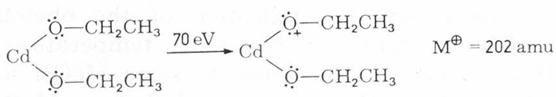
1.1. Ethoxide

$Cd(OEt)_2$ was placed in a melting point capillary tube. The transfer time when taken from the dessicator to the spectrometer was <2 min. Once placed in the solid probe assembly the sample was evacuated to 1.33×10^{-5} Pa at 298 K (25 °C) for about 3 min. During this time some volatile substance was emanated from the sample as noted by a pressure increase to 1.33×10^{-4} Pa. After the pressure returned to 1.33×10^{-5} Pa, and noting that the beam monitor showed little or no molecule ionization (vapor), the sample was heated to 323 K (50 °C) and a spectrum was run. After 1 min the sample was heated to 423—453 K (150—180 °C) and two spectra were run within 3 min. The pressure and beam monitor indicated that considerable gas was being evolved from the sample being heated. The sample was then heated to 453—473 K (180—200 °C) for 5 min with simultaneous decrease in pressure and beam monitor indication that the solid was decomposing to give off volatiles. The sample was then removed from the spectrometer. It was white, either CdO and/or $Cd(OH)_2$ or, possibly, undecomposed $Cd(OEt)_2$.

A repeated analysis was made on a new sample of $Cd(OEt)_2$. All observations stated for the first analysis were the same. This time, however, the sample was not removed from the spectrometer after the final heating at 473 K (200 °C) for 5 min. It was left in the spectrometer for 12 hrs at 473 K and 1.33×10^{-5} Pa. When removed from the spectrometer a part of the sample was brown (the part that was in closest contact with the heater coils) and a part remained white. The brown material is supposedly CdO.

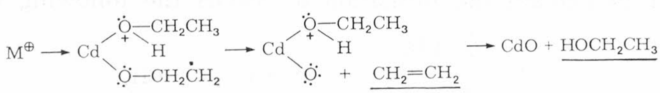
There are three possibilities for decomposition routes.

a) If $Cd(OEt)_2$ is volatile enough at 423 K/1.33×10^{-4} Pa (150°/10^{-6} torr), then vapor molecules of $Cd(OEt)_2$ could be ionized as follows.



(1)

M⊕ would then undergo a McLafferty rearrangement as follows.



(2)

The products underlined were both detected in these experiments. There is no detection of M⊕. It should be emphasized that this possibility a) is unlikely since $Cd(OEt)_2$ is probably not volatile at temperatures below that causing thermal decomposition.

b) The second possibility is thermal decomposition of $Cd(OEt)_2$ to give diethyl ether.

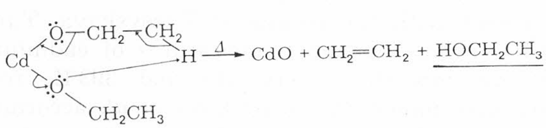
$$2\ \mathrm{Et\,O\,Cd\,O\,Et} \xrightarrow{\Delta} \mathrm{Et\,O\,Cd{-}O{-}Cd\,O\,Et} + \mathrm{Et{-}O{-}Et} \qquad (3)$$

or

$$\mathrm{Cd(OEt)_2} \xrightarrow{\Delta} \mathrm{CdO} + \mathrm{Et{-}O{-}Et} \qquad (4)$$

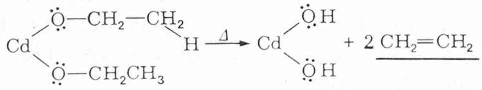
Neither of these seem to be operative under the conditions of the above experiments because no Et—O—Et was detected (no peaks at 73 or 59 amu).

c) Finally, thermal decomposition of $Cd(OEt)_2$ to give ethylene and/or ethanol.



(5)

or



(6)

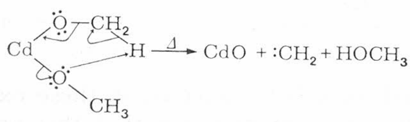
Possibility c(5) best fits the data. Both EtOH and $CH_2{=}CH_2$ were detected. The intensities of mass 31 ($CH_2{=}\underset{\cdot\cdot}{\overset{\oplus}{O}}H$ from EtOH) and mass 27 ($CH_2{=}\overset{\oplus}{C}H$ from $CH_2{=}CH_2$) peaks were used as criterions.

1.2. *Methoxide*

White $Cd(OMe)_2$ was placed in the spectrometer solid probe assembly, as in the method used for $Cd(OEt)_2$, and evacuated to 1.33×10^{-6} Pa/298 K (10^{-8} torr/25 °C) for 10 hrs. The sample was then inserted into the ionization chamber of the instrument, already heated to 423 K (150 °C).

Spectra were taken at time intervals of 1, 5, 20, 22, 35, 60, 90 min after insertion, while the sample was heated from 298 to 483 K (25 to 210 °C). At no time there were more than a few weak peaks detected. These were probably just increased background contamination. When the sample temperature exceeded 423 K (150 °C), the pressure increased and the beam monitor signal strengthened. Still, there was no indication of the obvious decomposition that was observed for $Cd(OEt)_2$ at the same temperature. Only at 473 K (200 °C) did $Cd(OMe)_2$ seem to decompose to some MeOH as indicated by a peak at 31 amu. No peak at 45 amu revealed that no MeOMe was evolved.

In order to explain the formation of MeOH the following is suggested:



(7)

The methylene produced (:CH_2) would probably be lost and not detected under the conditions of these measurements.

The sample was heated at 483 K (210 °C) for 1 hour and then removed from the instrument. Brown coloration indicated that the sample tube contained considerable CdO.

It should be pointed out that $Cd(OMe)_2$ decomposes at a higher temperature than $Cd(OEt)_2$ but once that temperature is reached methoxide decomposes faster than ethoxide to give CdO.

2. *DTA and X-ray Diffraction Study*

In the previous paragraph it was emphasized that $Cd(OMe)_2$ decomposes at a higher temperature than $Cd(OEt)_2$, but once that decomposition temperature is reached, methoxide decomposes faster than ethoxide. This observation is in agreement with the results of Turevskaya, Turova and Novoselova[1]. They found that the starting temperatures of cadmium methoxide and ethoxide thermal decomposition were 413 and 393 K, respectively. These temperatures were determined by Turevskaya *et al.* according to the method described by Shearer and Spencer[7]. In the present work the values found for these temperatures were somewhat higher than the ones obtained by Turevskaya *et al.*[1]. On the basis of mass spectrometry, DTA, and TG investigation we supposed that these temperatures are 443—453 K (170—180 °C) and about 423 K (150 °C), respectively.

DTA curves of Cd methoxide and ethoxide with some characteristic peak temperatures are shown in Figure 3. The numbers under given temperature data (or in parentheses), written in small figures, are the numbers of measurements. In the cases of 4 and more measurements standard deviations were calculated.

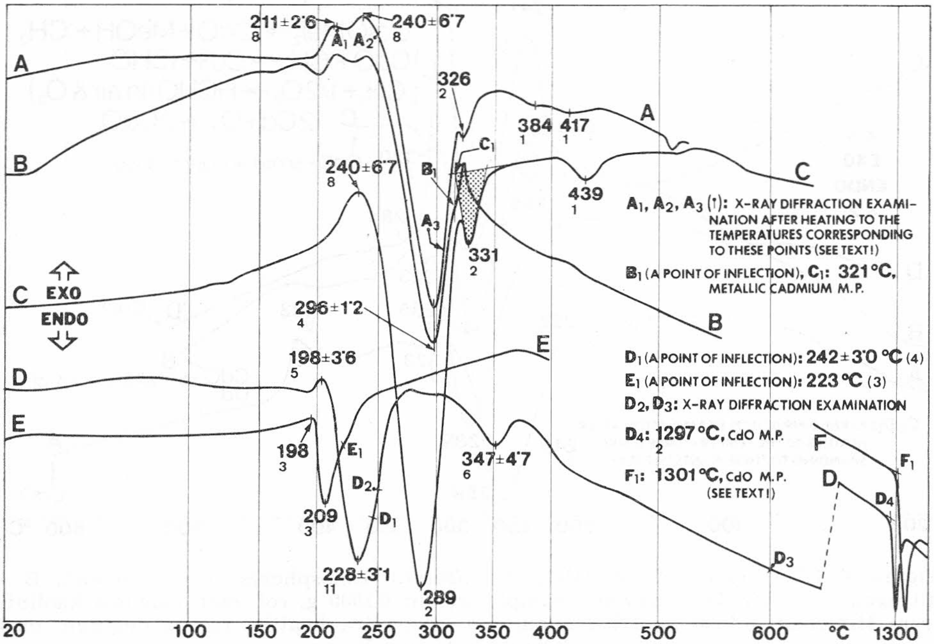


Figure 3. DTA curves of cadmium methoxide and ethoxide: A — $Cd(OMe)_2$ (1st preparation, 0.1000 g), ref. mat. SiO_2 (0.0650 g); B — $Cd(OMe)_2$ (1st preparation, 0.1000 g), ref. mat. Cd (0.0644 g); C — $Cd(OMe)_2$ (2nd preparation, 0.2000 g), ref. mat. calcined kaolinite from Hirschau, Federal Republic of Germany (0.2000 g); D — $Cd(OEt)_2$ (2nd preparation, 0.1000 g), ref. mat. calcined kaolinite from Hirschau (0.0800 g); E — $Cd(OEt)_2$ (1st preparation, 0.0180 g), ref. mat. α-Al_2O_3; F — CdO prepared by calcination of $Cd(NO_3)_2 \cdot 4H_2O$ »Mallinckrodt« Analytical Reagent (0.0650 g), ref. mat. SiO_2 (0.0650 g). DTA curves A, B, C, D, and F were obtained using DTA apparatus »Netzsch« (heating rate 5 deg/min, measuring range 50μ V, static air atmosphere). DTA curve E was obtained by Perkin-Elmer Thermoanalyzer (heating rate 5 deg/min, nitrogen atmosphere, 6700 Pa).

The number of peak temperature measurements is expressed by small figures below temperature data.

DTA traces A, B, and C belong to cadmium methoxide preparations. The most characteristic peaks are: exotherm at approx. 513 K (240 °C) and two endotherms at 562—569 K (289—296 °C) and 599—604 K (326—331 °C). The exotherm disappears in vacuum and in nitrogen atmosphere (Figure 4, DTA traces A and B). In oxygen it is much stronger than in air (Figure 4, DTA curves C and D). It seems that the endothermic effect of the reaction

$$Cd(OMe)_2 \rightarrow CdO + :CH_2 + CH_3OH$$

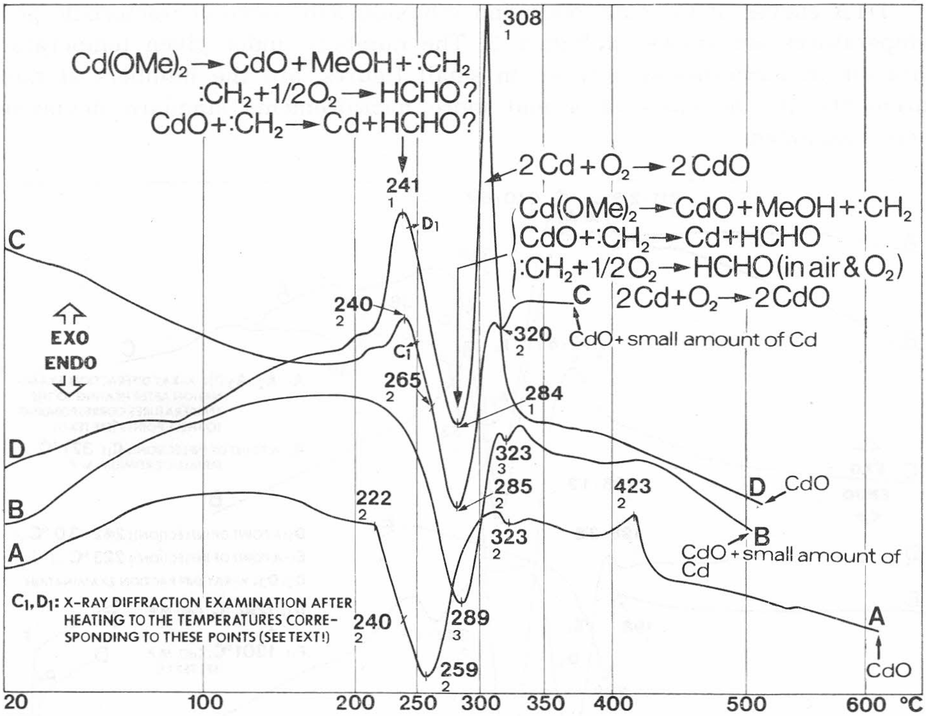


Figure 4. DTA traces of $Cd(OMe)_2$ in different atmospheres: A — vacuum, B — nitrogen, C — air, D — oxygen. Sample weight 0.1000 g, ref. mat. calcined kaolinite from Hirschau (0.1000 g), DTA apparatus »Netzsch«, heating rate 5 deg/min, measuring range 50 μ V.

in this part of decomposition is dominated by the exothermic effect of another supposed reaction. It should be pointed out that the exothermic effects observed below 523 K (250 °C) in air and, particularly, in oxygen are not the consequence of the ordering of $Cd(OMe)_2$ structure. X-ray examination of the residues after heating to the temperatures corresponding to points A_1, A_2 (Figure 3), and C_1, D_1 (Figure 4) did not show a structural change but merely a slight to small thermal decomposition of $Cd(OMe)_2$, indicated by a decrease of diffraction line intensities and, after DTA up to 523 K (250 °C), by the appearance of CdO diffraction lines (Figure 5). After heating of $Cd(OMe)_2$ at 513 K (240 °C) in air for 1 hr, CdO, the undestroyed $Cd(OMe)_2$, and several percent of $CdCO_3$ were found (Figure 5). These results are supported by the experimental evidence of $Cd(OMe)_2$ heating in oxygen at 453, 473, and 493 K (180, 200, and 220 °C), Table V.

Thermal decomposition of $Cd(OMe)_2$ is illustrated by the scanning electron micrographs of the residue after DTA in Figures 6 (nitrogen atmosphere; see also Figure 4, DTA curve B) and 7 (air; see also Figures 3 and 5).

It should be emphasized that only CdO was found in the residue after DTA in vacuum up to 885 K (612 °C), although an appreciate amount of Cd was formed by thermal decomposition of Cd methoxide (Figure 4, DTA

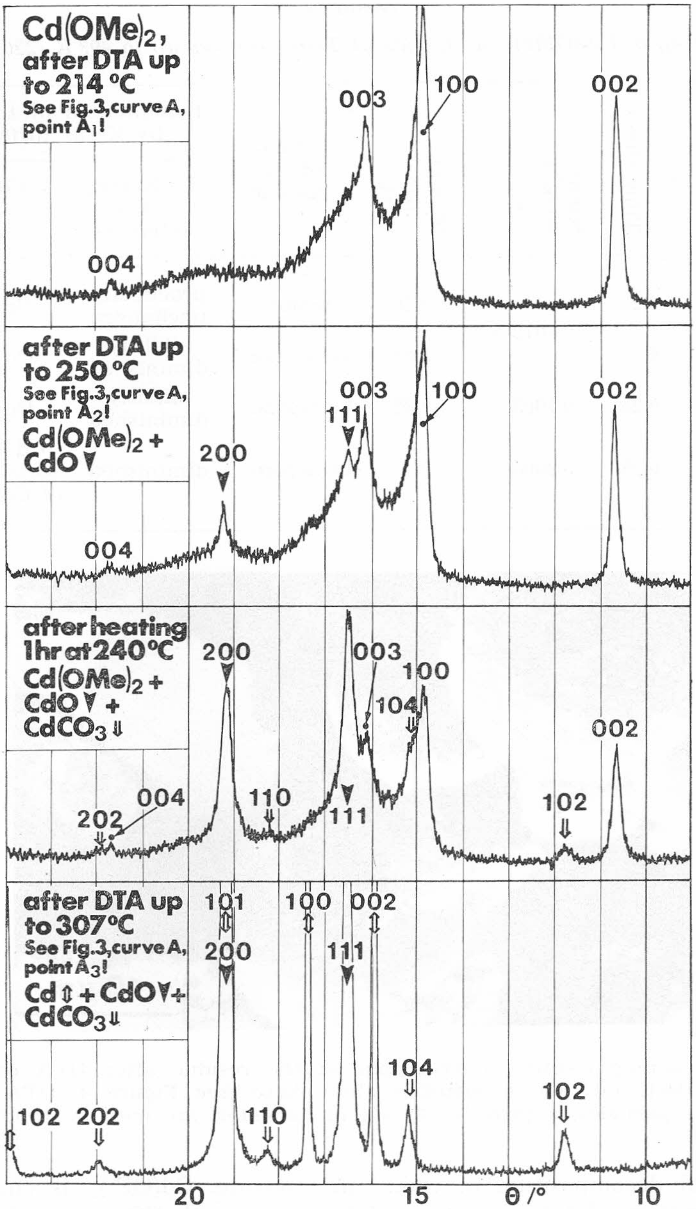


Figure 5. X-ray diffraction patterns of the residues after DTA of Cd(OMe)$_2$ run to different end temperatures in static air atmosphere (radiation: monochromatized Cu$K\alpha$).

curve A, endothermic effect caused by Cd melting at 596 K, i. e. 323 °C). This observation can be explained by the continuous evaporation of Cd melt during DTA in vacuum conditions. Strong exothermic effect at 696 K (423 °C) indicates the ordering in the structure of CdO.

TABLE V

Heating of Cd(OMe)$_2$ in Oxygen at Temperatures up to 493 K (220 °C)

Temperature K	Temperature °C	Time (hrs.)	Sample weight g	Weight loss %	Colour of the residue	Examination of the residue by X-ray diffraction: Diffraction line intensities	Examination of the residue by X-ray diffraction: Composition of the residue
453	180	0.25	0.1012	2.46	white	practically unchanged	Cd(OMe)$_2$
		8		3.01	yellowish	slightly diminished	Cd(OMe)$_2$
473	200	0.25	0.1003	2.82	yellowish	slightly diminished	Cd(OMe)$_2$
493	220	0.25	0.2000	2.50	brownish	diminished	Cd(OMe)$_2$ + some percents of CdO and Cd

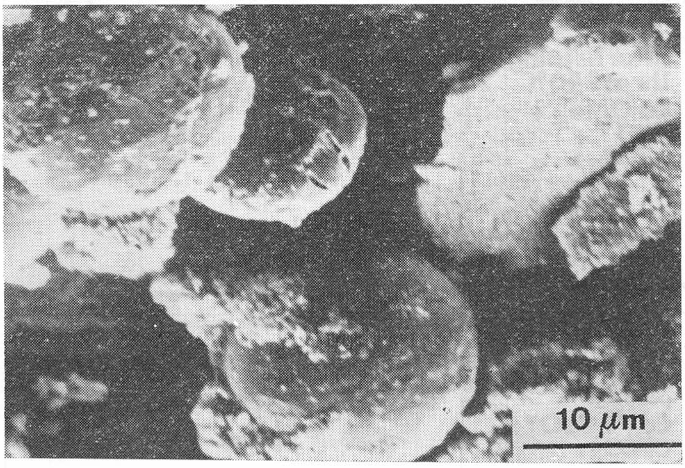


Figure 6. Scanning electron micrographs of the residue after DTA of Cd(OMe)$_2$ run up to 788 K (515 °C) in nitrogen atmosphere (see Figure 4, DTA curve B); spheric particles, approx. 7—15 μm in diameter, are metallic cadmium.

Thermal decomposition of cadmium ethoxide, Cd(OEt)$_2$, is characterized by the formation of CdO which partially reacts with CO_2 giving $CdCO_3$. The examination of the residue after DTA up to 523 K (250 °C) by X-ray diffraction (Figure 3, DTA curve D, point D$_2$) showed the presence of CdO and $CdCO_3$ (10—15%). The residue after DTA up to 873 K, i. e. 600 °C (Figure 3, DTA trace D, point D$_3$) was composed of CdO, $CdCO_3$ (about 5%), Cd (less than 1%), and an unidentified compound (less than 1%). Theoretical weight loss (36.60%) was not achieved even by DTA up to 1503 K (1230 °C). Actual weight loss at this temperature was 30.73%. Because of the presence

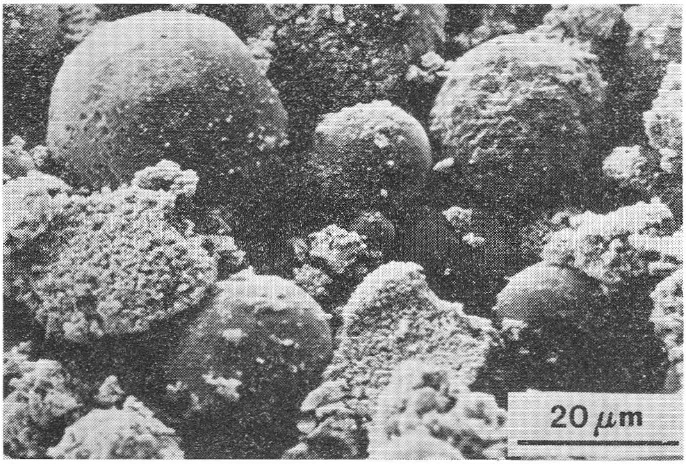


Figure 7. Scanning electron micrographs of the residue after DTA of $Cd(OMe)_2$ run up to 580 K (307 °C) in air (see the corresponding X-ray diffraction pattern in Figure 5); metallic cadmium (spheric particles, approx. 6—33 μm in diameter) is the main component.

of the above mentioned impurities the melting point of the residue obtained by thermal decomposition of $Cd(OEt)_2$ was found to be 1563 K, i. e. 1295 °C (Figure 3, point D_4). The melting point of pure CdO, prepared by thermal decomposition of $Cd(NO_3)_2 \cdot 4H_2O$ [8], was found to be 1574 K, i. e. 1301 °C (Figure 3, DTA curve F, point F_1). In the literature ref. 9. one can find that CdO melts above 1773 K (1500 °C).

All the results of DTA and X-ray diffraction study of cadmium methoxide and ethoxide thermal decomposition are collected in Table VI. It should be pointed out that the weight losses after DTA of $Cd(OMe)_2$ samples up to different end temperatures were influenced by partial (during DTA in air) or complete oxidation of Cd (during DTA in oxygen or in air up to 600 °C and more) and by evaporation of Cd melt. Theoretical weight loss 26.41 or 35.57% is in accordance with the assumption that the solid residue of $Cd(OMe)_2$ thermal decomposition is CdO or Cd, respectively.

In these investigations CdO, Cd, and $CdCO_3$ were easily identified by X-ray diffraction according to the data existing in the JCPDS Powder Diffraction File, Card. Nos. 5—640, 5—674, and 8—456, respectively[10].

In some samples CdO and $CdCO_3$ showed diffraction broadening due to the small crystallite size. This effect was analyzed by the method of integral widths (*e. g.* S. Popović[11] and the references therein) and by the Warren--Averbach deconvolution method[12]. In both methods the line profiles of CdO heated up to 873 K (600 °C) or to 1573 K (1300 °C) were used as instrumental broadening. In Figure 8 two X-ray diffraction lines of CdO produced by heating of $Cd(OEt)_2$ up to the temperatures of 523 K (250 °C) and 873 K (600 °C) are shown. The size of CdO crystallites in the residue after heating

TABLE VI

Thermoanalytical Data for Decomposition of Cadmium Methoxide and Ethoxide

Substance	Technique Atmosphere	Heating rate °C/min End temp. °C	Sample weight g	Weight loss %	Reference material Weight/g	Peak temperatures[a]/°C								Residue[b] (X-ray diffraction analysis)	Remark
Cd (OMe$_2$)	DTA[c] air (s)	5 525	0.1000	34.96	SiO_2 0.0650	211 Ex	240 Ex	296 En		326[d] En				CdO+(Cd)	Fig. 3, A
	DTA air (s)	5 307	0.1000	28.02	SiO_2 0.0650	212 Ex	235 Ex	296 En						Cd+CdO+ +$CdCO_3$	Fig. 5
	DTA air (s)	5 570	0.1000		Cd 0.0644	215 Ex	243 Ex	297 En						CdO+(Cd)	Fig. 3, B
	DTA air (s)	5 627	0.2000	36.45	H. K.[e] 0.2000		240 Ex	289 En		331 En			439 En	CdO+Cd+	Fig. 3, C
	DTA vac.	5 612	0.1000	29.10	H. K. 0.1000		222[f]	259 En		323 En		423[g] Ex		CdO	Fig. 4, A
	DTA N_2	5 514	0.1000	28.84	H. K. 0.1000			289 En		323 En				CdO+(Cd)	Fig. 4, B Fig. 6
	DTA O_2	5 525	0.1000	21.70	H. K. 1.000	210 Ex	241 Ex	284 En	308 Ex					CdO	Fig. 4, D
	DTA, TG air (s)	10 765	0.1800	25.94	α-Al_2O_3	215 Ex	270[h] Ex	315 En			380[i] Ex			CdO	

$Cd(OEt)_2$	DTA[j] N_2	5 400	0.0180	32.22	α-Al_2O_3	198 Ex	209 En			CdO	Fig. 3, E
	DTA air (s)	5 600	0.1000	23.96	H. K. 0.1500	196 Ex	226 En			$CdO + CdCO_3$[k] $+ Cd + X$	
	DTA air (s)	5 1400	0.1000	71.13	H. K. 0.0800	198 Ex	228 En	347 En	1295 En	CdO	Fig. 3, D
CdO[l]	DTA air (s)	5 1340	0.1000		SiO_2 0.0650				1301 En	CdO	Fig. 3, F

[a] — Ex = exothermic, En = endothermic effect;
[b] — (Cd) means few percents of Cd; Cd or CdO indicates the main component of the residue;
[c] — (s) means a static atmosphere in DTA furnace;
[d] — Melting of metallic cadmium;
[e] — Calcined kaolinite from Hirschau, Federal Republik of Germany (H. K.)
[f] — Initial temperature of $Cd(OMe)_2$ decomposition;
[g] — Ordering of CdO structure;
[h] — Point of inflection (weight loss at 270 °C, determined by TG, was 3.50%);
[i] — Partial oxidation of metallic cadmium proved by TG (weight gain was 0.56%);
[j] — DTA made by means of Perkin-Elmer Thermoanalyzer in low pressure nitrogen atmosphere (~6700 Pa); in all other analyses DTA apparatus »Netzsch« was used except the simultaneous DTA/TG which was made by means of Derivatograph;
[k] — The residue contained about 5% of $CdCO_3$, less than 1% of Cd, and less than 1% of an unidentified component X;
[l] — CdO sample prepared by the calcination of $Cd(NO_3)_2 \cdot 4H_2O$ »Mallinckrodt«, analytical reagent, at 1100 °C for 10 hrs. (weight loss was 59.54%, theoretical weight loss 58.38%).

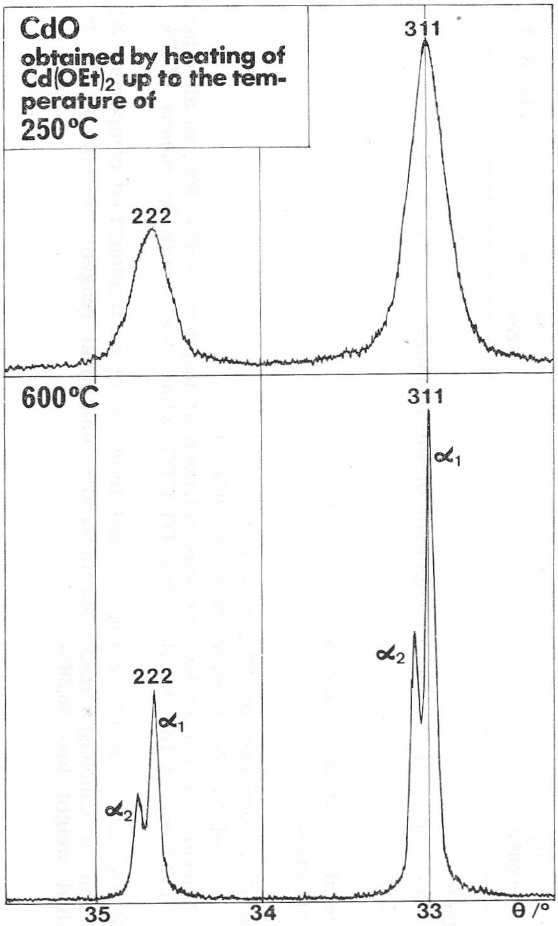


Figure 8. Two X-ray diffraction lines of CdO in the residue obtained by heating $Cd(OEt)_2$ up to 523 K (250 °C, broad lines) and 873 K (600 °C, sharp lines); radiation: monochromatized Cu*K*α.

of $Cd(OEt)_2$ up to 523 K (250 °C) is (20 ± 1) nm as obtained from the integral widths, and (18 ± 1) nm as derived by the Warren-Averbach method (Figure 9).

Stability of Cadmium Methoxide and Ethoxide in Air

The stability of $Cd(OMe)_2$ and $Cd(OEt)_2$ in air was studied by DTA and X-ray diffraction. Both compounds change to $CdCO_3$ via $Cd(OH)_2$. Identification of $Cd(OH)_2$ was based on the data existing in the JCPDS Powder Diffraction File, Card. No. 13—226[10].

Samples of $Cd(OMe)_2$ and $Cd(OEt)_2$ were left in closed containers (out of desiccator) for 80 days. The structure of Cd methoxide was destroyed with the formation of $Cd(OH)_2$ and poorly crystallized $CdCO_3$ (Figure 10,

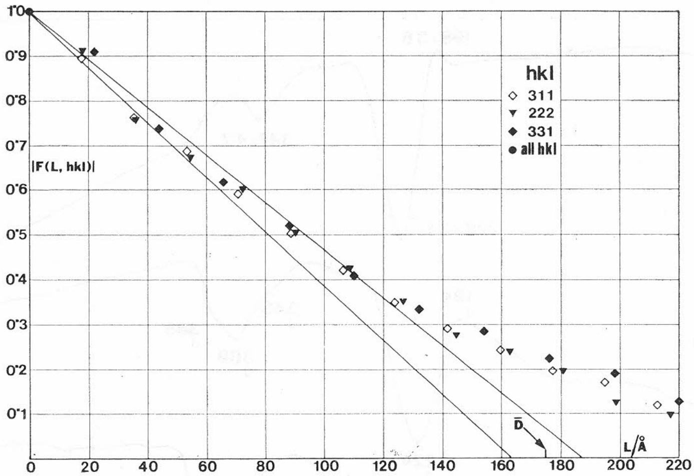


Figure 9. Fourier coefficients $|F(L, h\,k\,l)|$ for three X-ray diffraction line profiles of CdO heated up to 523 K, *i. e.* 250 °C (corrected for instrumental broadening) as the function of the distance L normal to the crystal lattice reflecting planes. The mean crystallite size is $\bar{D} = (18 \pm 1)$ nm.

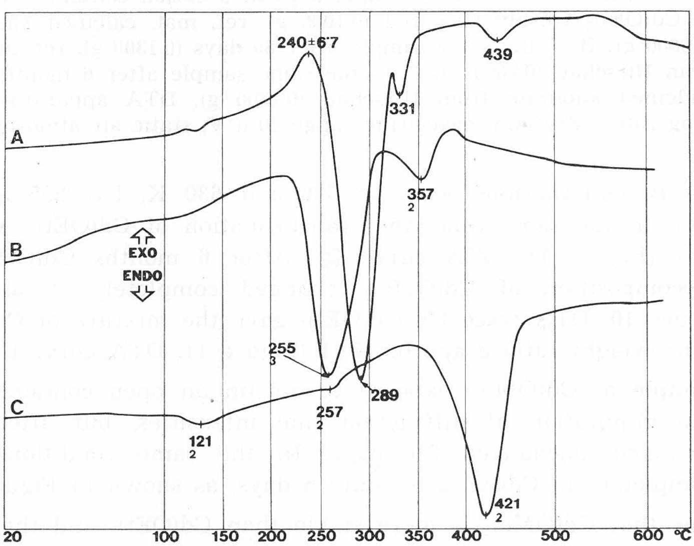


Figure 10. DTA traces of $Cd(OMe)_2$ sample kept in a closed container out of desiccator: A — $Cd(OMe)_2$ freshly prepared (0.2000 g), ref. mat. calcined kaolinite from Hirschau (0.2000 g); B — the same sample after 80 days (0.2000 g), ref. mat. calcined kaolinite from Hirschau (0.2000 g); C — the same sample after 6 months (0.1300 g), ref. mat. calcined kaolinite from Hirschau (0.1300 g). DTA apparatus »Netzsch«, heating rate 5 deg/min, measuring range 50 μV, static air atmosphere.

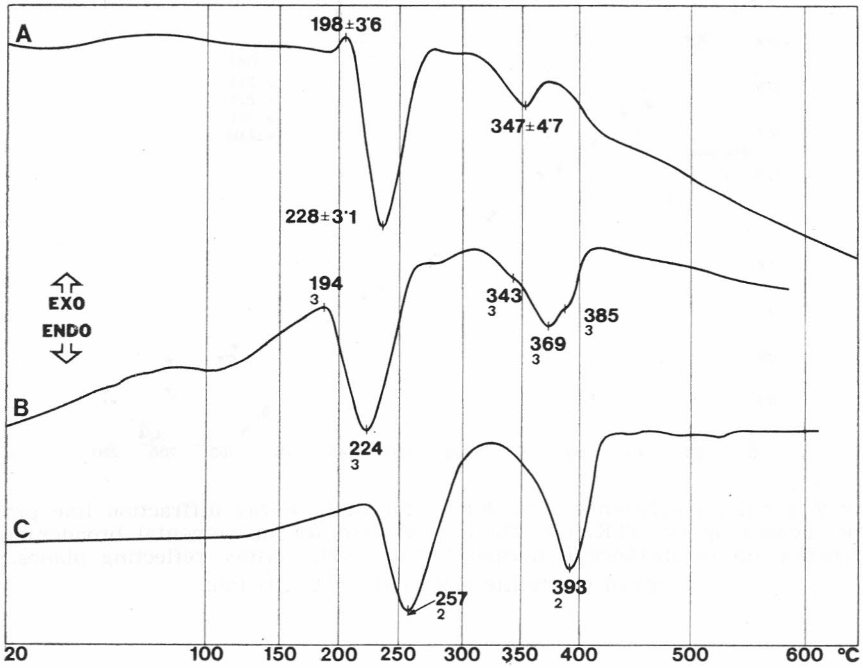


Figure 11. DTA curves of $Cd(OEt)_2$ sample kept in a closed container out of desiccator: A — $Cd(OEt)_2$ freshly prepared (0.1000 g), ref. mat. calcined kaolinite from Hirschau (0.0800 g); B — the same sample after 80 days (0.1300 g), ref. mat. calcined kaolinite from Hirschau (0.2000 g); C — the same sample after 6 months (0.1300 g), ref. mat. calcined kaolinite from Hirschau (0.1300 g). DTA apparatus »Netzsch«, heating rate 5 deg/min, measuring range 50 μ V, static air atmosphere.

DTA curve B, endothermic peaks at 528 and 630 K, i. e. 255 and 357 °C, respectively). In the same time, the transformation of $Cd(OEt)_2$ was remarkably lower (Figure 11, DTA curve B). After 6 months $Cd(OH)_2$, formed through decomposition of $Cd(OMe)_2$, changed completely to almost pure $CdCO_3$ (Figure 10, DTA trace C). $Cd(OEt)_2$ gave the mixture of $Cd(OH)_2$ and $CdCO_3$ in the weight ratio a approx. 1 : 1 (Figure 11, DTA curve C).

The sample of $Cd(OMe)_2$ exposed to air (in an open container) showed the starting diminution of diffraction line intensities, but after that the sample remained unchanged for days. In the same conditions $Cd(OEt)_2$ changed completely to $CdCO_3$ after only 6 days, as shown in Figure 12.

It seems that $Cd(OMe)_2$ is more stable than $Cd(OEt)_2$ and the sample is unchanged for a long time, but when decomposition of $Cd(OMe)_2$ takes place the change is very fast, probably faster than the transformation of $Cd(OEt)_2$.

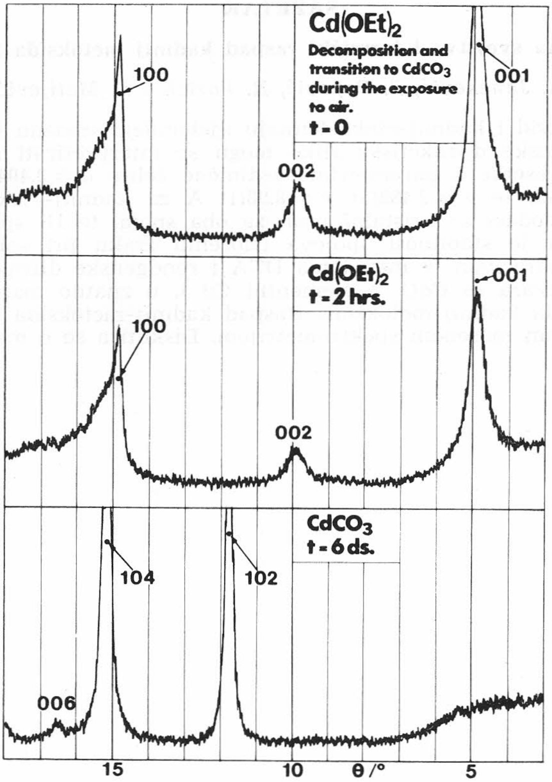


Figure 12. X-ray diffraction patterns of $Cd(OEt)_2$ exposed to air for 2 hrs. and for 6 days (radiation: monochromatized Cu*K*α).

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SAŽETAK

Struktura, kemijska svojstva i termički raspad kadmij metoksida i kadmij etoksida

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Kadmij-metoksid i kadmij-etoksid imaju djelomično sređenu kaotičnu slojevitu strukturu. Rendgenske difrakcijske slike mogu se interpretirati s pomoću heksagonske kristalne rešetke s parametrima jedinične ćelije a = 3,494(3), c = 8,36(1) Å za kadmij-metoksid, te a = 3,482(3), c = 8,98(1) Å za kadmij-etoksid. Određeni su difraktometrijski podaci za kristalni prah za oba spoja, te IR spektar za kadmij-etoksid. Istražena je stabilnost spojeva izloženih zraku pri sobnoj temperaturi. Termički raspad istraživan je metodama DTA i rendgenske difrakcije. Pri raspadu kadmij-etoksida stvara se CdO, a elementni Cd i, u znatno manjem udjelu, CdO produkti su raspada kadmij-metoksida. Raspad kadmij-metoksida i kadmij-etoksida također je istraživan masenom spektrometrijom. Diskutira se o mehanizmu raspada obaju alkoksida.