Journal of Thermal Analysis, Vol. 21 (1981) 27—34

THERMAL STUDIES OF ZINC AND CADMIUM HALIDE COMPLEXES WITH N-*TERT*-ALKYLACRYLAMIDES

J. ŻURAKOWSKA-ORSZAGH, K. MIROWSKI and H. WILCZURA

Department of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warszawa, Poland

(Received July 30, 1980; in revised form January 24, 1981)

The thermal properties of complexes of N-*tert*-butylacrylamide and N-*tert*-amylacrylamide with $ZnCl_2$, $ZnBr_2$, $CdCl_2$ and $CdBr_2$ have been studied in air and in argon by TG and DTA. The decomposition proceeds in two steps with evolution of simple, low molecular weight gaseous products. The use of various heating rates revealed an additional exothermic DTA peak for complexes with zinc and cadmium chlorides corresponding to a solid state polymerization reaction which was confirmed by IR spectral analysis. This effect was not observed for corresponding complexes of zinc and cadmium bromides, which show much lower thermal stability.

Numerous publications and several reviews [1—3] exist on the thermal decomposition of complexes of volatile, nonreactive ligands with inorganic salts. However, little attention has been given to the thermal behavior of complexes formed from polar monomers and inorganic salts. The only detailed studies refer to complexes of 4-vinylpyridine with $CoCl_2$ and $Co(NCS)_2$ [4, 5]. The thermal decomposition of these complexes proceeds by successive loss of volatile ligand without decomposition. At the same time polymerization occurs, which is competitive with the release of the monomer.

Our previous studies were mainly concerned with the solid state polymerization of large series of N-*tert*-alkylacryl-amides [6, 7]. Recently we have investigated the solid state polymerization of N-*tert*-alkylacrylamides complexed with $ZnCl_2$ [8], as well as the solid state copolymerization of ternary complexes: 4-vinylpyridine and N-*tert*-alkylacrylamide — $ZnCl_2$ [9].

The main purpose of the present investigation is the study of the thermal properties of complexes of N-*tert*-alkylacrylamides with zinc and cadmium halides of general formula $A_2 \cdot MX_2$, where A is N-*tert*-butylacrylamide (NtBA) or N-*tert*-amylacrylamide (NtAA), M is zinc or cadmium and X is chlorine or bromine.

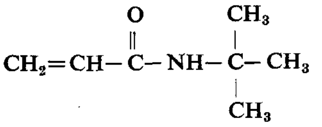
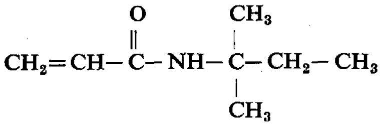
Experimental

Preparation of complexes

Complexes of N-*tert*-butylacrylamide and N-*tert*-amylacrylamide with zinc and cadmium halides were obtained from the corresponding amides and metal salts. The complexation reaction was carried out in ether solution for zinc halides and

Table 1

Characteristics of examined complexes

Amide	Salt	Molecular ratio amide : salt	Melting point, °C	Formulae abbreviation
N-*tert*-butylacrylamide	$ZnCl_2$	2 : 1	143	$(NtBA)_2 \cdot ZnCl_2$
 $CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}{-}CH_3$	$ZnBr_2$	2 : 1	132	$(NtBA)_2 \cdot ZnBr_2$
	$CdCl_2$	2 : 1	R	$(NtBA)_2 \cdot CdCl_2$
	$CdBr_2$	2 : 1	R	$(NtBA)_2 \cdot CdBr_2$
N-*tert*-amylacrylamide	$ZnCl_2$	2 : 1	99	$(NtAA)_2 \cdot ZnCl_2$
 $CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}{-}CH_2{-}CH_3$	$ZnBr_2$	2 : 1	109	$(NtAA)_2 \cdot ZnBr_2$
	$CdCl_2$	2 : 1	R	$(NtAA)_2 \cdot CdCl_2$
	$CdBr_2$	2 : 1	R	$(NtAA)_2 \cdot CdBr_2$

R — the complex decomposes without melting.

in ethanol solutions for cadmium halides. Synthesis of amides, preparation of complexes and the analysis procedures have been described in detail previously [10]. A list of complexes examined, molecular compositions, melting points and formula abbreviations are presented in Table 1.

Analysis with derivatograph

Thermal analysis was performed using the MOM model Q – Derivatograph (Paulik–Paulik–Erdey Hungary) [11, 12]. The experiments were carried out using porcelain crucibles and air and dynamic pure argon (15 l/hour) atmospheres over the temperature range 20 to 600°. Heating rates were 0.6, 1.25, 2.5, 5, 10 and 20°/min. Al_2O_3 heated previously at 1400°, was used as reference.

Infrared spectra

Infrared absorption spectra were recorded on a Specord 75 IR spectrometer (Carl Zeiss Jena DDR), using KBr discs, in the range 700–4000 cm^{-1}.

Pyrolysis

Pyrolysis of amides and complexes was performed at 250° in ampoules sealed under vacuum. Gaseous decomposition products were separated and identified using gas chromatograph type GChF 18.3 (Willi Giede DDR) using argon as a carrier gas and a thermoconductometric detector.

Results and discussion

The analysis of the thermal curves obtained for this series of complexes shows that for all complexes the general characteristics of thermal decomposition are similar, both in air and in argon. The TG and DTA curves obtained for thermal decomposition of $(NtAA)_2 \cdot ZnCl_2$ in argon and in air are representative of the series and are presented in Figs 1 and 2 respectively.

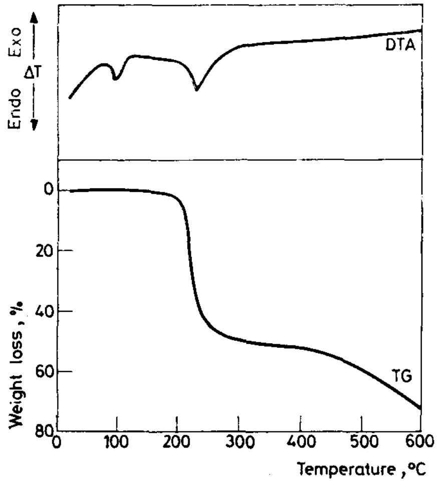


Fig. 1. DTA and TG curves for thermal decomposition of $(NtAA)_2 \cdot ZnCl_2$ in the flow of argon

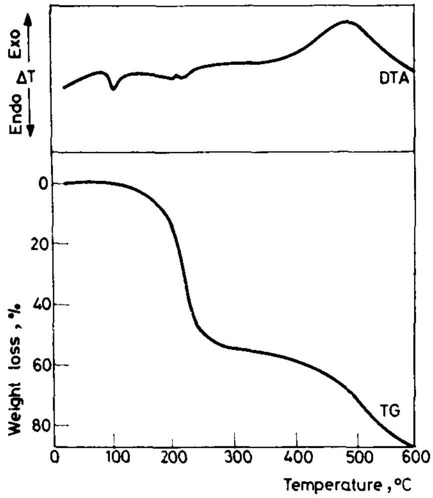


Fig. 2. DTA and TG curves for thermal decomposition of $(NtAA)_2 \cdot ZnCl_2$ in air

In both cases the decomposition proceeds in two steps, the first beeing very rapid, the second much slower. However the analysis of DTA curves shows distinct differences in the thermal effects. In argon the first step is strongly endothermic, while the second is very diffuse and does not show any marked thermal effect.

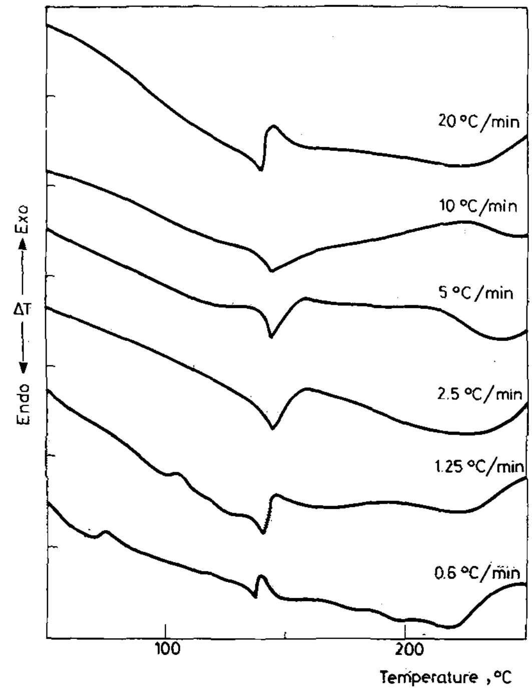


Fig. 3. DTA curves for thermal decomposition of $(NtBA)_2 \cdot ZnCl_2$ in the flow of argon at various heating rate

Conversely in air the first step endotherm is much smaller while the second is more pronounced and reflects the exothermic combustion of the gaseous decomposition products.

Special consideration has been given to the explanation of the characteristics of the two step decomposition. Examination of the mass loss corresponding to the first and to the second step of decomposition excluded the possibility of successive liberation of amide molecules bonded at the same coordination center.

For all complexes with zinc halides an additional DTA endotherm is observed due to melting of the complex (Figs 1 and 2). This endotherm is not shown by the corresponding cadmium halide complexes, since these decompose without melting (see Table 1).

The residue after thermal decomposition in air (up to 600°) is a white solid and contains the corresponding metal halide, while in argon the residue is higher and much darker and contains additionally some carbonized compounds composed mainly of carbon with traces of nitrogen (as shown by elemental analysis). For example in the case of $(NtAA)_2 \cdot ZnCl_2$ presented on Figs 1 and 2 the mass loss up to 600° in argon corresponds to 73% but in air the corresponding mass loss is 88%.

To obtain kinetic data relating to the thermal decomposition of these complexes a series of curves were obtained by heating the complexes in argon at various heating rates. It was found that for some complexes the change of heating rate has a strong influence on the character of DTA curves. As an example data obtained for $(NtBA)_2 \cdot ZnCl_2$ are presented in Fig. 3. As seen from this family of DTA curves, at low heating rates (0.6 and 1.25°/min.) a new exothermic peak appears, which is not observed at higher heating rates.

Data obtained from thermal studies with different heating rates for all the complexes are presented in Table 2.

As seen from this Table, for complexes $(NtBA)_2 \cdot ZnCl_2$ and $(NtAA)_2 \cdot ZnCl_2$ this peak appears before the endothermic peak corresponding to the melting of the sample. At the same time a decrease in temperature corresponding to initial mass loss is observed. It should be pointed out that $(NtBA)_2 \cdot CdCl_2$ and $(NtAA)_2 \cdot \cdot ZnCl_2$ do not melt and the exothermic peak appears before the decomposition. On the other hand for the complexes of amides with $ZnBr_2$ and $CdBr_2$ this peak was not observed even at the lowest possible heating rate.

It is suggested that the exothermic peak is connected with polymerization of the complex. This hyphothesis was fully confirmed by IR spectroscopy. Analyzed samples were heated to temperatures 5° below the beginning of and 5° above the end of the exothermic peak. The $C=C$ vibration band present for all the complexes [$(NtBA)_2 \cdot ZnCl_2$ 1630 cm^{-1}, $(NtBA)_2 \cdot CdCl_2$ 1628 cm^{-1}, $(NtAA)_2 \cdot ZnCl_2$ 1640 cm^{-1}, $(NtAA)_2 \cdot CdCl_2$ 1636 cm^{-1}], was not present for samples heated above the exothermic peak. Hence this DTA peak corresponds to the solid state polymerization of the complex. Conversely, for complexes submitted to higher heating rates the $C=C$ vibration bands were observed even for samples heated to temperatures just below the beginning of decomposition.

As seen from Fig. 3 and Table 2 the polymerization temperature increases with increased heating rate. For higher heating rates, the polymerization probably occurs simultaneously with decomposition which may explain why the thermal effect due to polymerization cannot be observed as a separate DTA peak.

In order to obtain more information concerning the decomposition of the complexes, the gas chromatography of pyrolysis products has been carried out. A remarkable difference in the behaviour of amides and their corresponding complexes was observed. In the case of pure amides, practically no gaseous product was obtained which is consistent with the high thermal stability of these compounds. Conversely under the same experimental conditions the complexes decomposed with evolution of gaseous products consisting of CO_2, lower aliphatic hydrocarbons, as well as small amounts of CO, N_2, H_2 and H_2O. This proves that in the presence of the complexing salt a decrease of bond strength of N-*tert*-alkylacryl-

Table 2

Characteristics of thermal decomposition of examined complex compounds (in the flow of argon)

Complex compound	Heating rate, °C/min	Melting point, °C	Exothermic peak (polymerization) temp. range, °C	Decomposition		Weight loss up to 300 °C, %
				initial temp., °C	temp. of max. rate, °C	
$(NtBA)_2 \cdot ZnCl_2$	0.6	135	65–88	74	226 b	45
	1.25	140	100–115	117	232	44
	2.5	145	a	220	241	43
	5	145	a	219	246	43
	10	146	a	200	248	43
	20	140	a	211	230	45
$(NtBA)_2 \cdot ZnBr_2$	0.6	127	a	110	180 b	35 c
	2.5	134	a	139	205	38
$(NtBA)_2 \cdot CdCl_2$	0.6	d	49–90	84	b	43 c
	2.5	d	a	85	160	51
$(NtBA)_2 \cdot CdBr_2$	0.6	d	a	70	130 b	46 c
	2.5	d	a	79	172	48
$(NtAA)_2 \cdot ZnCl_2$	0.6	100	74–90	100	b	19 c
	2.5	104	a	190	220	46
$(NtAA)_2 \cdot ZnBr_2$	0.6	108	a	108	183 b	37 c
	2.5	116	a	156	205	40
$(NtAA)_2 \cdot CdCl_2$	0.6	d	53–87	79	b	32 c
	2.5	d	a	88	170	45
$(NtAA)_2 \cdot CdBr_2$	0.6	d	a	78	b	31 c
	2.5	d	a	85	188	46

a — the sample does not polymerize before decomposition, the exothermal peak is not observed
b — the DTA curve is very diffuse
c — weight loss up to 200°
d — the sample does not melt

amide occurs, which can lead to decomposition of the monomers as well as the polymer formed during heating. The formation of the coordination bond metal-carbonyl oxygen has a strong influence on the rest of amide molecule because of the conjugation of the $C=O$ bond with the vinyl bond and the free electron pair on the nitrogen atom. The effect of the complexing salt on the electronic structure of N-*tert*-alkylacrylamide molecules has been explained more precisely in our previous publication [10].

The decomposition to low molecular weight products excludes the possibility of the ligand being released without decomposition which was reported by Agnew and Brown for the 4-vinylpyridine – $CoCl_2$ complex [4, 5]. Such pronounced difference in the behaviour of these two types of complex is directly related to the difference in structure between 4-vinylpyridine and N-*tert*-alkylacrylamides.

From Table 2 the following trends are evident. Complexes with cadmium halides show lower thermal stability than the corresponding complexes with zinc halides. Bromide complexes have lower thermal stability than chloride complexes with the same metal and the same amide.

In summary derivatography has proved to be very useful method for analysing solid complexes of polar vinyl monomers which exhibit thermal decomposition and polymerization. If polymerization is allowed for the present thermal data are in good agreement with those obtained by other methods [8, 10].

References

1. D. Dollimore, Differential Therm. Anal., 1 (1970) 427, Ed. by Robert C. Mackenzie, Academic London, England.
2. E. J. Segal, Festkoerperchemie 404 (1973), Ed. by V. Boldyrev, K. Meyer, Verlag Grandstoffind, Leipzig, DDR.
3. G. Liptay, Thermochim. Acta 15 (1976) 159.
4. N. H. Agnew and M. E. Brown, J. Polym. Sci., Polym. Chem. Ed. 9 (1971) 2561.
5. N. H. Agnew and M. E. Brown, J. Polym. Sci., Polym. Chem., Ed. 12 (1974) 1493.
6. J. Żurakowska-Orszagh, Polymer 19 (1978) 717.
7. J. Żurakowska-Orszagh, Polymer 19 (1978) 720.
8. A. Kaim and J. Żurakowska-Orszagh, Proceedings Int. Symp. on Macromolecules, 1977, Dublin, 1 p. 30.
9. W. Busz, A. Orszagh and J. Żurakowska-Orszagh, Proceedings Int. Symp. on Macromolecules, 1977, Dublin 1 p. 24.
10. J. Żurakowska-Orszagh, K. Mirowski and A. Kaim, J. Polym. Sci., Polym. Chem. Ed. in print.
11. F. Paulik, J. Paulik and L. Erdey, Z. Anal. Chem. 160 (1958) 241.
12. F. Paulik, L. Erdey and S. Gál, Z. Anal. Chem. 163 (1958) 321.

Résumé — On a étudié, par TG et ATD, dans l'air et l'argon, les propriétés thermiques des complexes du N-tertbutyl-acrylamide et du N-tétramylacrylamide avec $ZnCl_2$, $ZnBr_2$, $CdCl_2$ et $CdBr_2$. La décomposition s'effectue en deux étapes, avec dégagement de produits gazeux simples de faible poids moléculaire. L'application de différentes vitesses de chauffage a révélé, pour les complexes des chlorures de zinc et de cadmium, un pic exothermique additionnel en ATD qui correspond à la réaction de polymérisation dans l'état solide et qui a été confirmé par spectrométrie infrarouge. On n'a pas observé cet effet dans le cas des complexes correspondants des bromures de zinc et cadmium dont la stabilité thermique est bien plus faible.

Zusammenfassung — Die thermischen Eigenschaften der Komplexe von N-Tertbutylacrylamid und N-Tertamylacrylamid mit $ZnCl_2$, $ZnBr_2$, $CdCl_2$ und $CdBr_2$ wurden in Luft und in Argon durch TG und DTA studiert. Die Zersetzung verläuft in zwei Stufen unter Entwicklung einfacher gasförmiger Produkte niedriges Molekulargewichts. Der Einsatz verschiedener Aufheizgeschwindigkeiten zeigte für Komplexe mit Zink- und Cadmiumchloriden einen zusätzlichen DTA Peak, der Festphasen-Polymerisationsreaktion entsprechend, welche durch IR-

Spektralanalyse bestätigt wurde. Dieser Effekt wurde bei den entsprechenden Komplexen der Zink- und Cadmiumbromide, welche eine viel geringere Thermostabilität besitzen, nicht beobachtet.

Резюме — С помощью ТГ и ДТА изучено термическое разложение в атмосфере воздуха и аргона комплексов N-терт-бутилакриламида и N-третамилакриламида с $ZnCl_2$, $ZnBr_2$, $CdCl_2$ и $CdBr_2$. Процесс разложения протекает в две стадии с образованием простых, газообразных продуктов низкомолекулярного веса. Использование различных скоростей нагрева позволило обнаружить в случае комплексов с хлоридами цинка и кадмия необычного экзотермического ДТА пика. Пик соответствует реакции твердофазной полимеризации, которая была подтверждена ИК спектрами. Этот эффект не был обнаружен в соответствующих комплексах с бромидами цинка и кадмия, которые показали намного меньшую термическую устойчивость.