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THERMOANALYTICAL RESEARCH CARRIED OUT AT THE INSTITUTE OF INORGANIC CHEMISTRY OF TECHNICAL UNIVERSITY OF BUDAPEST

G. LIPTAY, G. KENESSEY, A. BORBÉLY–KUSZMANN and M. ERDŐSY

Institute of Inorganic Chemistry
Technical University H–1521, Budapest

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Abstract

Thermoanalytical studies have been going on at the Institute of Inorganic Chemistry for nearly 20 years. The present paper wishes to introduce the results of three main fields of the investigations. Primarily, the goal of our studies was the production of complexes of transient metals with ligands containing different N-atoms and also the study of the obtained compounds with other analytical methods. On the other hand the thermal stability of inorganic polymers (especially the silicone-rubber and polyethylene) was examined, ageing estimations were done, and their dependence on the method of their production and on the pre-treatment processes modelling their possible application circumstances were investigated. Finally, the application of thermal investigations to solve various industrial problems was introduced, particularly in the territory of quality-tests of materials.

Keywords: thermoanalysis, complexes, silicones, polyethylene.

Introduction

Thermoanalytical investigations have been carried out at the Institute of Inorganic Chemistry since the mid-seventies. The thermal investigations focus on the following areas:

A) study of inorganic compounds and complexes
B) study of polymers (silicone, polyethylene)
C) enlargement of the thermoanalytical methods.

More than 80 publications at home, several domestic and international lectures, co-operations with some foreign researchers and research-institutes indicate the success of work in several fields of studies and methods. The investigations have practical importance as well. The thermal group of the Institute worked out more than 30 research reports for industrial companies.

A) The thermal study of complexes focuses on $M(py)_yX_2$ – type compounds where M: intermediate metal, py: pyridine or substituted pyridine derivative, X: halogen [1].

This series of compounds gradually decompose in a thermal way, the ligands leave without cracking, the intermediate compounds can be prepared both thermally and studied by other instrumental analytical methods as well. So, studying the intermediates got by decomposition valuable information can be obtained about the structure of complexes, the mechanism of decomposition and in some cases about their kinetics, too.

Our systematic investigations started with Cd-compounds [2–5], as oxidation is not likely to occur in this case. On preparing the complex it was found that the solvent has only a low-rate effect on the number of ligands of the product. In case of methyl-substituted pyridines, at α–picoline with 1, β–picoline usually with 2, γ–picoline with 4 ligands can the complex be prepared. *Fig. 1* shows the thermal decomposition of $Cd(\gamma\text{–}pic)_4Cl_2$ as an example.

During gradual decomposition at first 2, later 1 picoline leaves. Then one-third picoline leaves stoichiometrically, which refers to a polynuclear intermediary. This sample was prepared in a thermal way (with a sudden freezing of the decomposition process) and in this way a compound was obtained we had not got before. Far infrared and X-ray examination (within the frame of a Swedish co-operation) was carried out on these compounds and information about their structure and change of structure was obtained.

Studying the Zn-picoline halogenides it was found that the complexes melted [1], so the decomposition was taking place in liquid-phase (dragging), an intermediary cannot be prepared.

Studying Co-complexes it was found that during melting, the proportion of ligand and metal affects the composition of the product formed. With varying the proportion a product could be produced (number of ligands 1, 2/3) that was believed earlier to be produced in a thermal way only [6].

So, the contradiction occurring in the literature can be explained where the production of fractional ligands was introduced. They came into being as coincident mixture of whole-number ligands.

During treatment of samples in a vacuum drying pistol it was found that the ligands partly leave in a reversible way. Their reversibility was tried not only with lost ligands but with ligands substituted at another place as well. In this way even ternary complexes containing β– and γ–picolines could be obtained. These compounds are completely new ones [7]. A sample with a low-rate ligand produced in a vacuum drying pistol is able to bind another type of picoline from vapour-phase so that it could

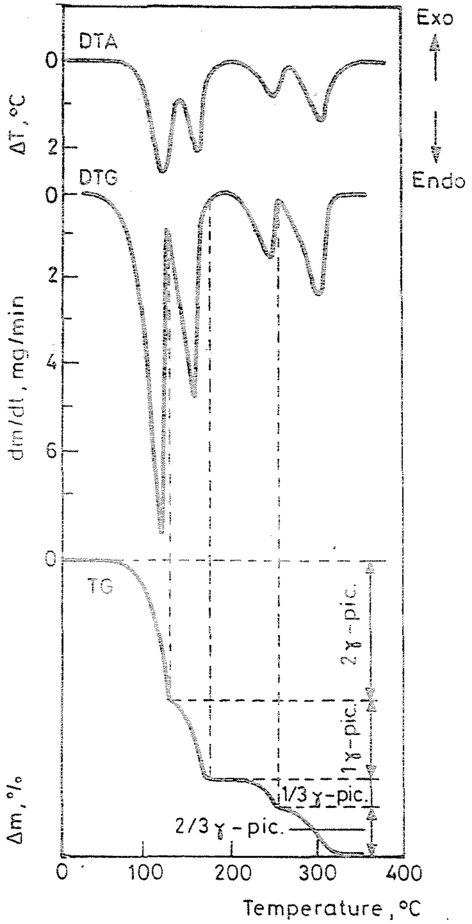

Fig. 1. Thermal decomposition of Cd(γ–pic)$_4$Cl$_2$

be substituted with a ligand binding much stronger. *Fig. 2* shows the thermoanalytical decomposition curves of Co(γ–pic)$_2$(β–pic)$_2$Cl$_2$ produced in this way.

In case of the complex, leaving of the first 2 mols of ligands takes place in a lower temperature interval than in case of Co(γ–pic)$_4$Cl$_2$, similar to the first step of Co(β–pic)$_4$Cl$_2$. The complex melts at the same time with losing its two ligands, its endotherm DTA-sign is overlapping with the endotherm process of decomposition, so an independent peak cannot be observed. The run of the derivatogram curve is analogous with that of the thermal intermediary Co(γ–pic)$_2$Cl$_2$. The existence of 'mixed' complexes was supported with far infrared examinations.

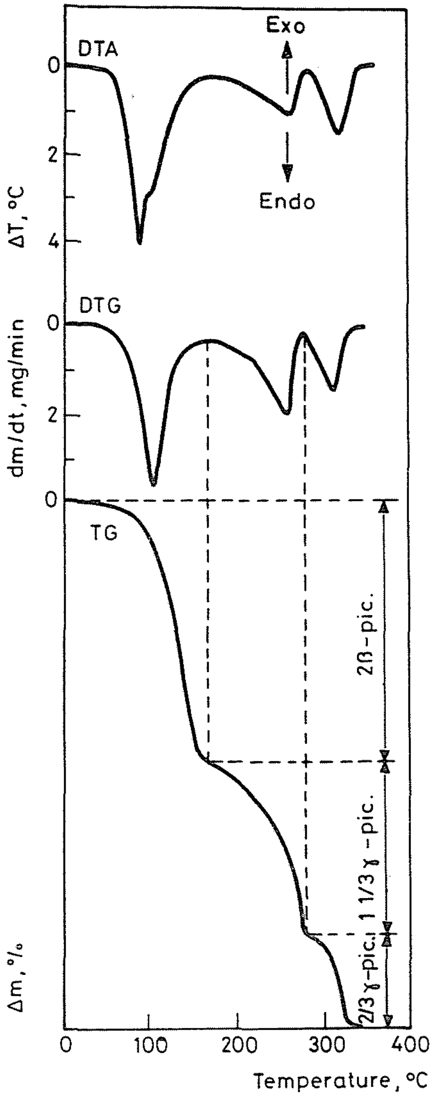

Fig. 2. Thermal decomposition of Co(γ-pic)$_2$(β-pic)$_2$Cl$_2$

Diol-type complexes were investigated beside co-ordinated covalent complexes. The Institute of Inorganic and Analytical Chemistry of JATE was studying the complexes of transient metal-sulphate with ethyleneglycol, we joined their thermoanalytical studies. *Fig. 3* shows the decomposition of some zinc-complexes.

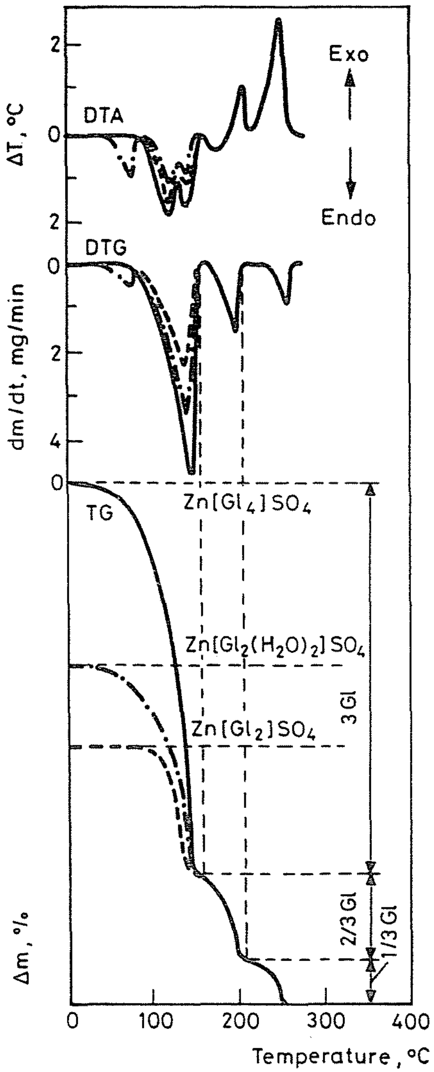

Fig. 3. Thermal decomposition of some Zn–glycol complexes. Gl means glycol as the ligand

During the decomposition of all complexes up to 150°C an intermediary containing 1 ligand is produced which decomposes in two steps — formally losing 2/3 then 1/3 mol glycol — to $ZnSO_4$, exotherm DTA effect can be observed. The reason for exothermicity can be the combustion of the leaving ligand around the sample. The intermediary ($Zn(gl)_{1/3}SO_4$) with a fractional stoichiometrical exponent can be a polynuclear complex

Table 1
Summary of co-operation partners in the study of compounds and complexes

Cation	Ligand	Anion	Co-operation partners	Literature
Cd	Picoline	Halogenid	Arrhenius Laboratory, Stockholm	[2–6]
Ni	Pyridine	Thiocianate	Technical University, Bratislava	[8]
Fe Cu Mn, Zn	Etylenediol Etylenediol Etylenediol	Sulfate Sulfate Sulfate	J. A. Univers. of Sciences, Szeged	[9], [10]
Alkaline, Alkaline earth	—	Dithionate	Babes–Bolyai University, Cluj	[11], [12]
Zn	Ammonium	Dithionate	Technical University, Helsinki	[13]
Co	Diamine	Halogenid	Babes–Bolyai University, Cluj	[14]
Intermediate metal	Dioximineamin			[15], [16]
Co		Thiocianate		[17]
Ni	Water Heavy water	Sulfate	Chemical University, Sofia	[18]
Zn, Fe, Ni, Ca, Sr, Ba	Water Heavy water	Chloride, Sulfate, Iodate		[19]
Fe		Hydroxide	Wien University	[20]

similar to the above-mentioned picoline-complexes. *Table 1* summarizes the co-operation partners in studying various complexes.

B) Inorganic polymers and other types of polymers were studied in the past years.

The main field of investigations of our Institute was the thermal study of organosilicon compounds and primarily the thermal stability of silicone-rubbers was examined.

Beside dynamic heating measurements isotherm thermogravimetry was applied. With the help of it we obtained results of practical importance as well [21–24]. A significant part of the work was carried out within the frame of the co-operation with the Wacker Chemie GmbH. These results will not be presented here, they will be a subject of another publication.

The thermal stability of insulating materials is a very important factor. In the course of our investigations we got in connection with different polyethylene (PE) cable insulators. The investigations carried out with the Hungarian Cable Works can be utilized in the production of high-tension cables. It was shown that PE containing only treating stabilizers are the most temperature-resistant (the electric properties of the sample containing voltage-stabilizing additives improve but its temperature-resistance decrease). The mechanical properties of the cross-linked PE are substantially better but weight loss takes place in PE on the effect of temperature increasing [25–27]. *Fig. 4* plastically summarizes all of these changes.

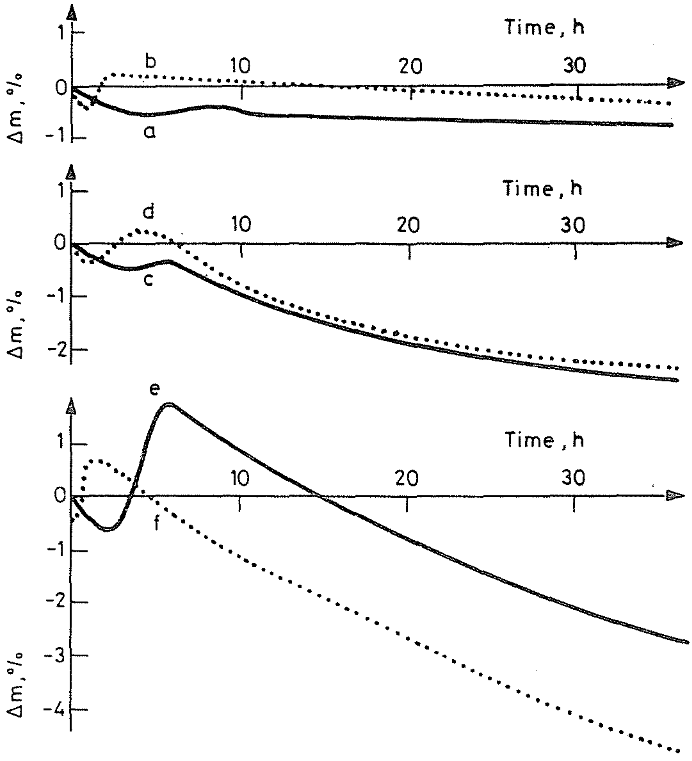

Fig. 4. Isothermal curves of electrically aged polyethylene obtained at 150°C *a*) polyethylene of basic quality, *b*) electrically aged polyethylene of basic quality, *c*) voltage-stabilized polyethylene, *d*) electrically aged, voltage stabilized polyethylene, *e*) cross-linked polyethylene, *f*) electrically aged, cross-linked polyethylene

The isothermic thermogravimetric curves of samples treated in electric field are indicated by a dashed line in the figure. It can be seen that the decomposition process will be shorter in time on the effect of electric field, which can be suitable for examinations of ageing of samples in electric field.

Initial weight loss can be observed on the S-shaped horizontal curves, which is followed by a significant weight growth caused by oxidation (especially in case of the cross- linked sample). After a maximum weight loss can be observed where PE degradation is registered besides oxidation effects taking place in the sample. The isotherm gives the resultant curve of consequent processes. With the help of the curves details can be concluded concerning the extent of ageing of the samples and in some cases the degree of the heat- treatment during technological processes. E. g. the isotherms of the granular, once- and twice-compressed PE samples are numerically different.

The curves of dynamic investigations of PE samples are very similar to each other, but from the kinetic evaluations of curves measured with different heating speed valuable information was obtained as regards the ageing of samples [28], which is good for establishing relative sequences.

Dilatometric [29] and DSC measurements [30] of PE-types resulted in data of practical importance with the help of French and German cooperations.

C) Other fields of application

The enlargement of field of application and working out methods were also parts of our task during the last years. The list of topics shows that widening of application of thermal analysis is still an important problem even today. The investigations consisted of the thermal analysis of catalysts [31], beam-treated foods [32], electrodes of accumulators — with the determination of PbO_2– contents [33] — of inorganic salts of premixers [34], and gaschromatographic charges [35].

In the course of our studies the question of weight and surface proportion arose which can command a general interest.

The introduced samples show how effectively the thermal analysis can be applied in the examination of inorganic compounds, complexes and polymers and how wide the new field of application of thermal methods is, respectively.

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Address:

György LIPTAY,
Gábor KENESSEY,
Anna BORBÉLY–KUSZMANN and
Miklós ERDŐSY,
Institute of Inorganic Chemisty
Technical University H–1521 Budapest
Hungary