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THERMOGRAVIMETRIC INVESTIGATION OF THE DECOMPOSITION OF AQUO-ACIDO COMPLEXES UNDER QUASI-ISOTHERMAL AND QUASI-ISOBARIC CONDITIONS

III. BINUCLEAR EDTA CHELATES

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The dehydration processes of some binuclear EDTA chelates were investigated under the conditions of the recently developed method of quasi-isothermal – quasi-isobaric thermogravimetry, i.e. by means of the Q-Derivatograph. By applying different types of sample holder, it proved possible to change the partial pressure of the gaseous decomposition products in contact with the sample between 0.01 and 1.0 atm. On the basis of the curves obtained a series of conclusions were drawn regarding the kinetics, mechanism and equilibrium conditions of the dehydration processes. It was established that under the conditions applied a series of intermediates are formed transitionally, whose existence could not be identified by conventional thermoanalytical methods·

We earlier reported results obtained in investigations of the dehydration processes of EDTA chelate complexes of the type $M_IM_{II}L \cdot 9H_2O$ [1] and $M_IM_{II}L \cdot 6H_2O$ [2]. The examinations were carried out with the recently developed method of quasi-isothermal and quasi-isobaric thermogravimetry [3, 4]. Since we found the method to be suitable for the investigation of similar questions, we have studied in the same way the dehydrations of $Cu_2L \cdot 4H_2O$, $Zn_2L \cdot 6H_2O$ and $Ca_2L \cdot 7H_2O$. All three compounds are binuclear complexes, but only the structures of the first two are known:

$$[(H_2O)_2CuLCu(H_2O)_2] \text{ and}$$

$$[Zn(H_2O)_4O_IO_{II}]\,[ZnL]\,2H_2O$$

where O_I and O_{II} are the carbonyl oxygen atoms of the carboxylic group of EDTA; the EDTA in the Zn chelate is octodentate.

Experimental

Instrument

A Q-Derivatograph (Hungarian Optical Works, MOM Budapest) was used, by means of which thermoanalytical investigations can be performed under conventional [5] and quasi-isothermal and quasi-isobaric conditions [3, 4].

Experimental conditions

Curves 1–4 in Figs 1–3 were traced by applying a quasi-isothermal heating programme (0.5 mg weight change/min) and four different types of sample

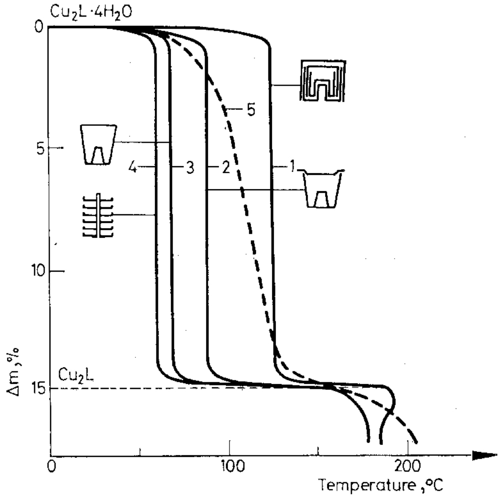

Fig. 1. Dehydration of EDTA chelate $Cu_2L \cdot 4H_2O$. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1–4: quasi-isothermal; decomposition rate: 0.5 mg/min; curve 5: dynamic; heating rate: 5°/min. Weight of sample: *ca.* 440 mg. Atmosphere: air

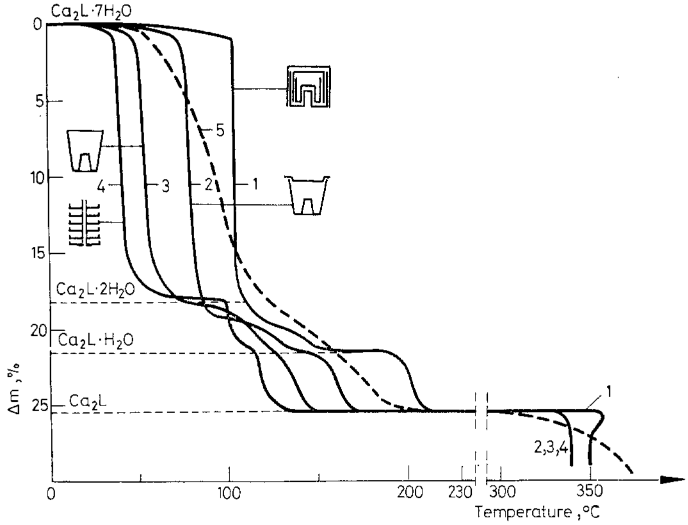

Fig. 2. Dehydration of EDTA chelate $Ca_2L \cdot 7H_2O$. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1–4: quasi-isothermal. Weight of sample: ca. 300 mg. Atmosphere: air

holders, i.e. the labyrinth crucible [3, 4], the conventional crucible of the derivatograph either covered or uncovered and the polyplate sample holder [5], which were applied in the sequence of curves 1–4, respectively. It was found that the partial pressure of the gaseous decomposition products in contact with the solid sample changed in the above sequence as follows: $P_{\text{gas}} = 0.01$, 0.05,

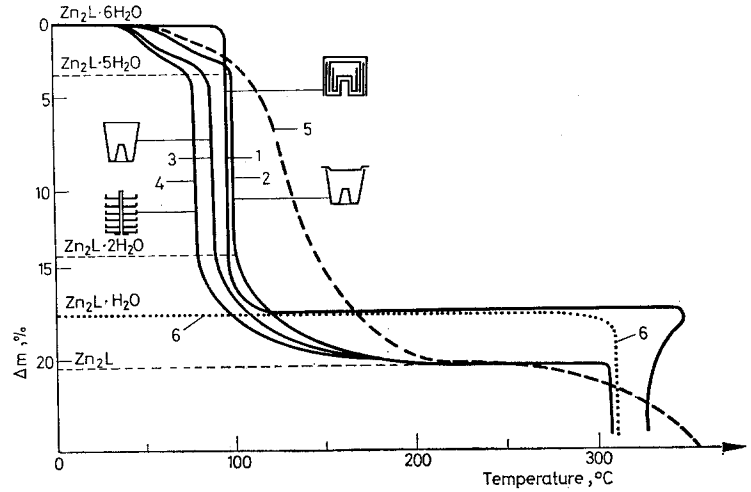

Fig. 3. Dehydration of EDTA chelate $Zn_2L \cdot 6H_2O$. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1–4: quasi-isothermal. Weight of sample: ca. 400 mg. Atmosphere: air. Curve 6: the conditions of this separate experiment are described in detail in the text

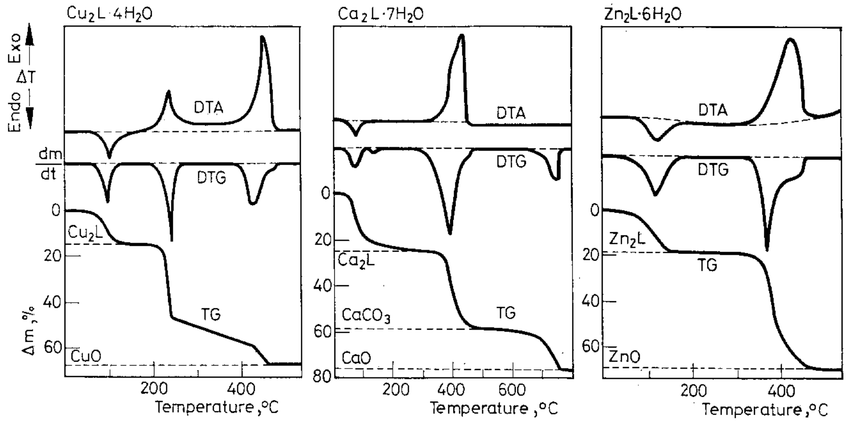

Fig. 4. TG, DTG and DTA curves of EDTA chelates. Sample holder: crucible without lid. Heating programme: dynamic, 5°/min. Weight of samples: ca. 250 mg. Atmosphere: air

0.2 and 1 atm respectively [1]. For the sake of comparison, the TG curve (curve 5) is shown by a dotted line in the figures. This curve was obtained in the conventional way by using the uncovered crucible and a heating programme of 5°/min. The TG, DTG and DTA curves in Fig. 4 demonstrate the whole thermal decomposition similarly in the uncovered crucible and under dynamic heating conditions. All experiments were carried out in the presence of air.

Chemicals

The complexes were prepared by precipitation from solution in accordance with well-known methods [6, 7]. The scheme of the reaction is:

$$2M(NO_3)_2 + Na_4L \xrightarrow[\text{medium}]{\text{aqueous}} M_2L \cdot nH_2O + 4NaNO_3$$

Results and discussion

$Cu_2L \cdot 4H_2O$

According to curve 1 in Fig. 1, the compound lost its 4 moles of water simultaneously at 125° without the formation of any intermediate. The process took place in the three other sample holders in a similar way (curves 2, 3 and), i.e. even when the partial pressure of the water vapour in contact with the sample was significantly decreased (from $p_{H_2O} = 1$ to $p_{H_2O} = 0.01$ atm). The decomposition temperature remained practically constant during the entire process in all four cases. The only difference between them was that their values decreased in accordance with the decreased partial pressure of water vapour. The stabilization of the transformation temperatures and the dependence of their values on the concentration of the gaseous decomposition products prove that the transformation leads to equilibrium. The stabilization of the decomposition temperature also means that the reaction took place according to zero order [1]. The complex probably lost its 4 moles of water simultaneously because it is of symmetrical structure.

$Ca_2L \cdot 7H_2O$

According to curve 1 in Fig. 2, the decomposition of the compound took place gradually. First $Ca_2L \cdot 2H_2O$, and then $Ca_2L \cdot H_2O$ was formed. The first decomposition process took place at about 105° without a significant change in this temperature value. Accordingly, this first reaction leads to equilibrium and can be qualified as a zero-order reaction, in contrast to the next two decomposition processes. Under the given circumstances $Ca_2L \cdot 2H_2O$ is not stable and its existence can be deduced only with difficulty from the course of the curve. The decomposition of $Ca_2L \cdot H_2O$ started only at 200°, but this process is not unambiguous and its order differs from zero.

An unusual correlation can be observed in the course of curves 1, 2, 3 and 4: while a higher partial pressure of water vapour seems to promote the formation of the compound containing less water, $Ca_2L \cdot H_2O$, a lower partial pressure seems to be more favourable for the formation of $Ca_2L \cdot 2H_2O$, containing more water. So far no acceptable explanation of this phenomenon has been found.

$Zn_2L \cdot 6H_2O$

Curve 1 in Fig. 3 offers a simple and unambiguous picture of the decomposition of the sample. It transformed at 95° in a zero-order reaction leading to equilibrium to $Zn_2L \cdot H_2O$, which remained strictly weight constant up to 360°. When the substance attained this temperature, it suddenly and totally decomposed without the transitional formation of Zn_2L. In contrast, in the case of curves 2, 3 and 4 the water content of the chelate decreased below the composition of $Zn_2L \cdot H_2O$ at about 100°, and at about 200–250° the chelate became totally waterfree. However, the anhydrous chelate remained stable only up to about 300°, whereupon it suddenly decomposed.

It is also noteworthy that according to curves 2, 3 and 4 the mechanism of the thermal decomposition was quite different from that demonstrated by curve 1. In the former cases the $Zn_2L \cdot 6H_2O$ transformed in a non-zero-order reaction into the intermediate $Zn_2L \cdot 5H_2O$, which then decomposed in a zero-order reaction leading to equilibrium. The remaining material still contained about 1–2 moles of water, which subsequently escaped in a broad temperature interval of about 150°.

With the two kinds of decomposition mechanism the contradiction can also be explained that the vertical section of curve 1 shows a lower temperature than curve 2, in spite of the fact that the partial pressure of the water vapour was five times higher in the labyrinth than in the covered crucible. However, this contradiction is only an apparent one since it is justified that the decomposition of a compound takes place at different temperature values and via different mechanisms if the experimental conditions are changed, and due to this different intermediates are formed:

$$p_{H_2O} = 1 \text{ atm:}$$

$$Zn_2L \cdot 6H_2O \xrightarrow{-5H_2O} Zn_2L \cdot H_2O \xrightarrow{-H_2O} Zn_2L$$

$$p_{H_2O} = 1 \text{ atm:}$$

$$Zn_2L \cdot 6H_2O \xrightarrow{-H_2O} Zn_2L \cdot 5H_2O \xrightarrow{-3H_2O} Zn_2L \cdot 2H_2O \xrightarrow{-2H_2O} Zn_2L$$

Curve 6, traced by a different measuring technique than the other curves, is suitable for study of the "cell effect". This curve was obtained in the following way. The $Zn_2L \cdot 6H_2O$ was examined first using the labyrinth crucible and the quasi-isothermal heating programme as in the case of curve 1. But at 150° the furnace was lifted, so that the sample was suddenly cooled down and the decomposition reaction was "frozen". In this way an intermediate of composition $Zn_2L \cdot H_2O$ was obtained (curve 1). There after the sample was transferred into the open crucible and the examination was restarted under quasi-isothermal conditions, as in the case of curve 3. Curve 6 was obtained as the result of this experiment. This curve proves the substance to be completely weight-stable up to 200° and practically weight-stable up to 310° in spite of the circumstance that under similar conditions the sample lost even the last traces of its water content by 200° if the starting compound was $Zn_2L \cdot 6H_2O$ (curve 3). This indicates that in the case of curves 2, 3 and 4 no $Zn_2L \cdot H_2O$ was formed, while it also strongly suggests that the decomposition of $Zn_2L \cdot H_2O$ was delayed by the "cell effect". In other words, in the case of curves 1 and 6 the last water molecule was retained due to steric hindrance as a consequence of the dense structure of the $Zn_2L \cdot H_2O$, even after splitting of the $Zn-OH_2$ bond.

Gore and Wendlandt [8] observed the "cell effect" in connection with the dehydration of hydroxyquinoline and methylhydroxyquinoline complexes.

In the present case the existence of the "cell-effect" seems to be supported by the fact that the rehydration of $Zn_2L \cdot H_2O$ similarly encounters difficulty. It is well known that $Zn_2L \cdot 6H_2O$ separates from a saturated solution of this compound at 25°, and $Zn_2L \cdot H_2O$ at 50°. Cooling-down of the solution to 25° is in vain as the once-separated $Zn_2L \cdot H_2O$ is not rehydrated even in the course of several days.

As can be seen from curves 5 in Figs 1–3, the results, obtained under the conventional experimental conditions, i.e. by applying the dynamic heating programme and the open crucible do not furnish similar information regarding the decomposition mechanism as in the case of the above-described examples.

The TG, DTG and DTA curves in Fig. 4 demonstrate the decompositions of the investigated chelates up to 600–800° under the conventional experimental conditions. It is conspicuous how unstable the anhydrous chelate Cu_2L is. It decomposed with maximum rate even at 230°, in contrast with the chelates Ca_2L and Zn_2L, which decomposed only at 400° and 380°, respectively. The splitting-off of the EDTA anion ligand in the decomposition of these complexes is a very complicated process similarly to the decomposition of organic materials. The exothermic peak of the DTA curve proves that the presence of air causes combustion to play a part in the process. The compositions of the residues were in accordance with expectations.

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Résumé — On a étudié le processus de la déshydratation de plusieurs chélates binucléaires de l'EDTA, en conditions quasi-isothermes et quasi-isobares, à l'aide d'un Derivatograph-Q. En utilisant des supports d'échantillon de divers types, les auteurs ont réussi à faire varier la pression partielle des produits de décomposition gazeux entre 0.01 et 1.0 atm au voisinage de l'échantillon. Des conclusions sur la cinétique, les conditions d'équilibre et le mécanisme des processus de déshydratation ont été déduites des courbes obtenues. Dans les conditions appliquées, on montre que des produits intermédiaires se forment transitoirement, dont l'existence ne peut pas être décelée par les méthodes conventionnelles de l'analyse thermique.

Zusammenfassung — Der Dehydratisierungsvorgang einiger binuklearer EDTA-Chelate wurde unter quasi-isothermen quasi-isobaren Bedingungen mit dem Q-Derivatographen untersucht. Mit der Anwendung von Probenträgern verschiedener Typen gelang es den Verfassern, den Partialdruck der gebildeten gasförmigen Zersetzungsprodukte in der Umgebung der festen Probe zwischen 0.01 und 1.0 Atm. zu ändern. Aufgrund der erhaltenen Kurven konnten einige Folgerungen in Bezug auf Kinetik, Mechanismus und Gleichgewichtsbedingungen der Dehydratisierungsvorgänge gezogen werden. Es wurde gezeigt, daß unter den angewandten Bedingungen vorübergehend Intermediäre entstehen, dern Existenz mit den konventionellen thermoanalytischen Methoden nicht nachgewiesen werden konnte.

Резюме — Авторы исследовали процессы дегидратации некоторых двухядерных ЕДТА хелатов в условиях недавно разработанного метода квази-изотермической — квази-изобарной термогравиметрии т. е. посредством Q-дериватографа. Применяя различные типы держателей образцов, авторы достигли изменения парциального давления газообразных продуктов разложения контактирующего образца между 0,01 и 1,0 атм. На основании полученных кривых был сделан ряд выводов, касающихся кинетики, механизма и равновесных условий процессов дегидратации. Установлено, что в данных условиях образуются переходные промежуточные продукты, существование которых не было идентифицировано обычными термоаналитическими методами.