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THERMOGRAVIMETRY UNDER QUASI-EQUILIBRIUM CONDITIONS UTILIZED IN THE STUDY OF THE THERMAL DISSOCIATION OF COMPOUNDS

I. Study of the kinetics of thermal dissociation for multi-stage reactions

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Study of the kinetics of multi-stage thermal dissociation reactions is a difficult task. Utilization of thermogravimetry under quasi-equilibrium conditions allows determination of intermediate phases, and if necessary their separation, in order to permit study of the kinetic stability separately. Parallel utilization of thermogravimetry under linear heating and quasi-equilibrium conditions allows detection of the existence of intermediate metastable phases.

Traditional thermoanalytical techniques have constantly been improved throughout the years; however, they invariably rely on linear heating. A vast amount of information on the thermal decomposition of individual compounds (temperature of onset of decomposition, number of decomposition steps, compositions of intermediate phases, temperature intervals of existence (stability) of intermediate compounds) has been accumulated by this technique. A survey of the characteristics of thermal analysis performed under linear heating demonstrates that the information obtained refers only to the kinetic stability of the compounds. In particular, if the sensitivity of the temperature sensor is constant, the temperature of the onset of decomposition for a number of compounds will – to a first approach – be the temperature at which one and the same rate constant of the reaction is reached (the value of this rate constant depending, of course, on the sensitivity of the instrument).

This particular feature of the technique (its "kinetic character" as it were), imprints its stamp on all conclusions.

A new thermoanalytical technique, the Q-derivatographic technique, was recently developed; this allows the thermogravimetric study of thermal decomposition reac-

tions under quasi-equilibrium (quasi-isobaric, quasi-isothermal) conditions [4, 5]. In this series of papers we intend to consider the novel potentials opened up by the Q-derivatographic technique in the study of reversible decomposition reactions, such as the thermal dissociation of coordination compounds during which a volatile ligand is split off:

$$A_s \rightleftharpoons B_s + C_{gas}$$

The methods existing at present for the mathematical processing of kinetic curves of thermal decomposition processes under non-isothermal conditions usually have the aim only of finding the best description of the process by some topochemical equation [1, 2]. For reversible thermal dissociation reactions of coordination compounds, the decomposition process is generally located on the surface of the particle. If the start ($0.05 \leqslant \alpha \leqslant 0.30$), the main part ($0.30 \leqslant \alpha \leqslant 0.80$) and the end ($0.80 \leqslant \alpha \leqslant 0.95$) of the process are analyzed separately, it will become possible to separate the range where the reaction proceeds on the interphase boundary (usually at values of $\alpha \approx 0.05$ to 0.50) from the range of diffusion kinetics: diffusion of the gas from the centre of the particle across a thick layer of product to the surface ($\alpha > 0.50$ to 0.60) [3].

The difficulties in the kinetic analysis of such processes increase sharply if the chemical reaction of thermal dissociation consists of a number of non-separated subsequent stages. Almost insuperable difficulties arise in determining the kinetic characteristics of each stage, for instance, when there is overlapping of the temperature intervals for the diffusion range of stage I and the kinetic range of stage II. The search for the true kinetic description of the process is extremely difficult, and it is highly questionable whether the found solution is unique.

If the stages of the reaction are not taken into consideration at all, and the overall kinetic curves (TG, DTG, DTA, EGD) are processed by standard methods, this will yield incorrect kinetic parameters [1].

Therefore, in studies of the kinetics of thermal dissociation reactions of coordination compounds, it is preferable to perform additional investigations to analyze whether stages are involved in the reaction, in order to ensure the reliability of the constants found. Information regarding the theoretical possibility of thermodynamically stable intermediate phases may be obtained by utilizing thermogravimetry under quasi-equilibrium conditions [4–6]. For this purpose it is usually sufficient to increase the pressure of the gaseous reaction product up to 1 atm (decomposition in the labyrinth sample holder). It is important to find out subsequently to what extent these phases are stable under conditions far from equilibrium (it is necessary to study kinetics under the "limiting vacuum" [7]: at evolved gas pressures below 10^{-3}–10^{-5} Torr).

In the following, the most frequent and relatively simple cases of multistep and multistage thermal decomposition reactions will be discussed with the aid of factual examples.

Experimental

EDTA chelates, i.e. aqua-acido complexes (descriptions of their synthesis are given in [8. 9]), complexes of aniline and its derivatives (synthesis according to [10]) and platinum(II) and palladium(II) complexes [12, 13] were studied.

Kinetic experiments were performed with a continuous reactor [3] (evolved gas detection method). The sample (10 mg) was placed on a porous support in a tubular holder, heated linearly at a rate 4 to 6 degree/min; helium was passed through the sample at a flow rate of 80 to 120 cm^3/min, and the bell-type gas evolution curve was recorded *versus* temperature (temperature was measured within the sample). A conductometric detector was used. A close fraction of particles (0.2 mm $\leqslant d \leqslant$ 0.4 mm) was used in the experiments.

This mode of running the experiments ensured reduced diffusion hindrance, performance of the process far from the equilibrium state and minimum self-cooling of the sample.

Experimental data were processed on a computer, using the program TA IB [1, 8]; the kinetic equation was selected via the linear function $\log g(\alpha)$ *vs.* $1/T$ (mechanisms with values $10^4 \geqslant A > 10^{24}$ were discarded as unlikely). The values of E and A were calculated from five experiments; experimental errors were calculated for the confidence limit of 95%.

The Q-derivatograph was used to perform thermogravimetry under quasi-isobaric, quasi-isothermal conditions.

Results and discussion

(i) An intermediate phase thermodynamically stable within a significant temperature interval exists even at low pressures of the gaseous reaction product

Dehydration of the EDTA chelate $CaNiL \cdot 4\,H_2O$ (L^{4-} is the anion $C_{10}H_8N_2O_8^{4-}$) under quasi-equilibrium conditions proceeds stepwise, with the formation of the intermediate hydrate $CaNiL \cdot 2.5\,H_2O$ (Fig. 1). During dehydration in the continuous reactor, the stages of the process are also sharply separated:

(I) 309–390 K $CaNiL \cdot 4\,H_2O \rightarrow CaNiL \cdot 2.5\,H_2O + 1.5\,H_2O$

(II) 409–507 K $CaNiL \cdot 2.5\,H_2O \rightarrow CaNiL + 2.5\,H_2O$

Stage I: equation of a compressible sphere ($0.04 \leqslant \alpha \leqslant 0.43$),

$$E = 106 \pm 5 \text{ kJ}, \quad \log A = 13.4 \pm 0.6$$

Stage II: equation of a compressible sphere ($0.05 \leqslant \alpha \leqslant 0.35$),

$$E = 149 \pm 13 \text{ kJ}, \quad \log A = 14.3 \pm 1.6$$

The difference in kinetic stability between the two hydrates in the dehydration process is due only to the energy barrier, since the two dehydration processes are isoentropic.

The above case is the simplest of all; full separation of the two stages of the process (both under experimental conditions close to equilibrium and under "limit vacuum" conditions) causes no difficulties in the interpretation of the two-step process.

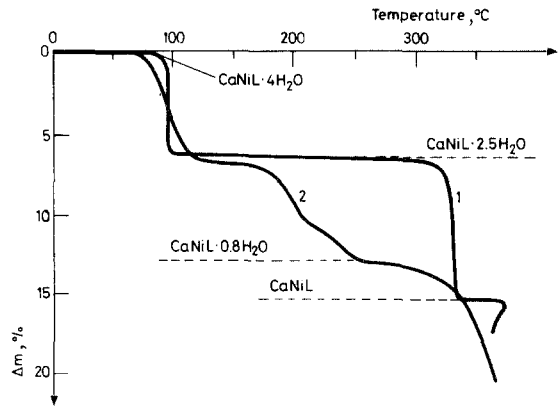

Fig. 1 Dehydration of the EDTA chelate CaNiL • 4 H_2O. Sample holder: labyrinth holder (1) and open crucible (2). Heating program: quasi-isothermal; sample mass: 250 mg; atmosphere: air

(ii) An intermediate metastable phase exists

We studied the dehydrochlorination processes of pyridine–platinum(II) and pyridine–palladium(II) complexes [12]:

$$(PyH)_2[PtCl_4] \rightleftharpoons [PtPy_2Cl_2] + 2\ HCl$$

$$(PyH)_2[PdCl_4] \rightleftharpoons [PdPy_2Cl_2] + 2\ HCl$$

Under quasi-equilibrium conditions, the study demonstrated the existence of an intermediate phase $(PyH)[PdPyCl_3]$, stable only at hydrogen chloride pressure around 1 atm (Fig. 2). In the decomposition of the complex $(PyH)_2[PtCl_4]$ under such conditions, no analogous stable intermediate $(PyH)[PtPyCl_3]$ is formed (Fig. 3). However, thermal analysis during linear heating yields DTA and DTG curves with inflexions, indicating a two-stage process [13].

A study of dehydrochlorination of the platinum(II) complex in the continuous reactor, at a heating rate of 5 degree/min, allowed distinct separation of two reaction stages. The two peak areas relating to evolved gas (391–445 K and 445–483 K) are practically equal, and consequently each stage corresponds to the evolution of one molecule of HCl (Fig. 4). Obviously, in the experiments with linear heating far from equilibrium conditions, the process of introducing pyridine into the internal sphere of the complex proceeds through a metastable intermediate $(PyH)[PtPyCl_3]$ corre-

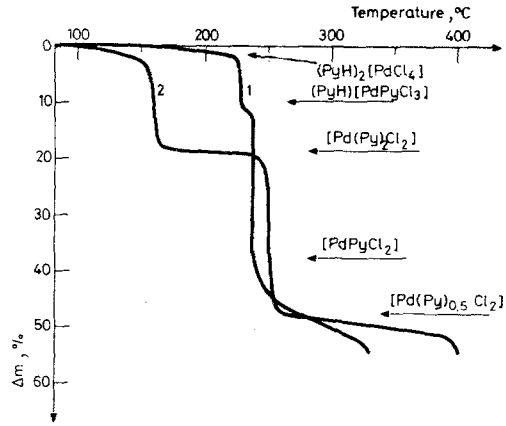

Fig. 2 Thermal dissociation of the complex $(PyH)_2[PdCl_4]$ [12]. Sample holder: labyrinth holder (1) and open crucible (2). Heating program: quasi-isothermal; sample mass: 200 mg, atmosphere: air

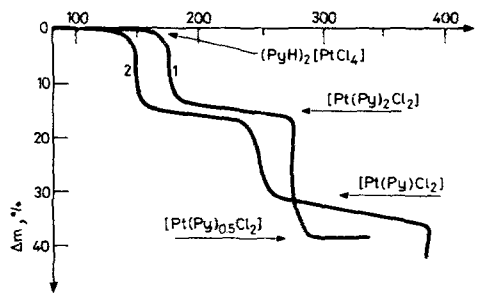

Fig. 3 Thermal dissociation of the complex $(PyH)_2[PtCl_4]$ [12]. Sample holder: labyrinth holder (1) and open crucible (2). Heating program: quasi-isothermal; sample mass: 200 mg; atmosphere: air

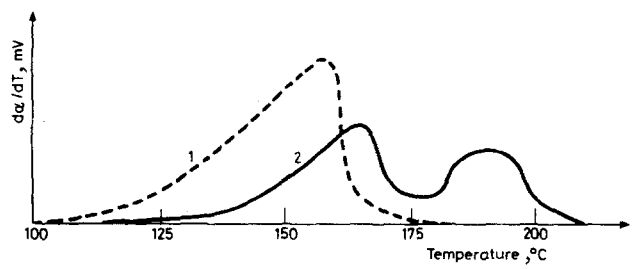

Fig. 4 Gas evolution curves in the decomposition of the complexes $(PyH)_2[PdCl_4]$ (1) and $(PyH)_2[PtCl_4]$ (2). Sample mass: 10 mg; sample holder: tubular; helium flow through the sample: 110 ml/min; heating rate: 5 degree/min; detector: conductometric

sponding to the Ostwald rule [14, 15]. Under quasi-equilibrium conditions, this intermediate is decomposed irreversibly to $[PtPy_2Cl_2]$. Increase of the pressure of HCl up to 1 atm (with the use of the labyrinth sample holder) cannot increase its thermodynamic stability; however, its kinetic stability is such that it allows accumulation of the intermediate in observable amounts during the decomposition of $(PyH)_2[PtCl_4]$ in the temperature interval 391–445 K (~ 10 min at a heating rate of 5 degree/min).

The particularity of this case is that one can study thermodynamic stability only for the reaction

$$(PyH)_2[PtCl_4] \rightleftharpoons [PtPy_2Cl_2] + 2\,HCl$$

and kinetic stability for the reaction

$$(PyH)_2[PtCl_4] \rightleftharpoons (PyH)[PtCl_3] + HCl$$

(equation of a compressible sphere,

$$0.005 \leqslant \alpha \leqslant 0.53,\ E = 128 \pm 6\ \text{kJ},\ \log A = 11.8 \pm 0.6)$$

The parallel utilization of the "kinetic" and "quasi-equilibrium" variants offers a unique possibility to record the metastable intermediate phase.

(iii) A thermodynamically stable intermediate phase exists at high temperatures only at high pressures (≈ 1 atm) of the volatile ligand, i.e. the gaseous product of the reaction

When the intermediate is separated, it is fairly stable at ambient temperature in a closed container (where the equilibrium pressure of the gas is established by partial decomposition). If decomposition of the initial complexes is studied far from the equilibrium state (in an inert gas flow), this phase will not be recorded in the decomposition curve.

We studied the thermal dissociation of zinc and nickel sulfate complexes with *m*-toluidine: $[ZnSO_4(m\text{-tol})_2]$ and $[NiSO_4(m\text{-tol})_2]$. Decomposition of the zinc compound under quasi-equilibrium conditions (Fig. 5a) proceeds in two steps, and the complex $[ZnSO_4(m\text{-tol})]$ is stable in the interval $p_{amine} = 0.05-1$ atm. In the case of the nickel complex, no plateau appears at $p_{amine} = 1$ atm in the mass loss curve, but an inflexion is observable at a loss of 1 molecule of toluidine. The existence of the phase $[NiSO_4(m\text{-tol})]$ within an observable temperature interval is apparently feasible only at $p_{amine} > 1$ atm.

When the amine pressure is lowered, the separation into steps is even less distinct (Fig. 5b); no temperature stabilization is observable. This is possibly related partly to the significant high-temperature pyrolysis of the ligand (the experiment lasts for more than three hours), which is not observed in the decomposition of $[ZnSO_4(m\text{-tol})_2]$.

To allow further studies, we synthetized the complex $[NiSO_4(m\text{-tol})]$ by an independent path and followed its decomposition under quasi-equilibrium conditions.

The kinetic parameters for decomposition in the continuous reactor were as follows:

$$[NiSO_4(m\text{-tol})_2] \rightleftharpoons NiSO_4 + 2\ m\text{-toluidine},$$

equation of a compressible sphere, $0.05 \leqslant \alpha \leqslant 0.54$, $T_0 = 444 \pm 6$ K, $E = 148 \pm 6$ kJ, $\log A = 12.9 \pm 0.6$.

$$[NiSO_4(m\text{-tol})] \rightleftharpoons NiSO_4 + m\text{-toluidine},$$

equation of a compressible sphere, $0.05 \leqslant \alpha \leqslant 0.50$, $T_0 = 329 \pm 5$ K, $E = 145 \pm 6$ kJ, $\log A = 18.4 \pm 0.7$.

At 444 K, the decomposition rate constant k_2 for the complex $[NiSO_4(m\text{-tol})_2]$ is $10^{-4.5}$, whereas the corresponding value k_1 for the complex $[NiSO_4(m\text{-tol})]$ is $10^{1.3}$. For this reason, the latter complex cannot accumulate, and the decomposition should be considered a one-stage process:

$$[NiSO_4(m\text{-tol})_2] \rightleftharpoons NiSO_4 + 2\ m\text{-toluidine}$$

The different kinetic stabilities of these two complexes are related to the entropy factor only, since the activation energies of the thermal dissociation processes are equal (isoenthalpic reactions).

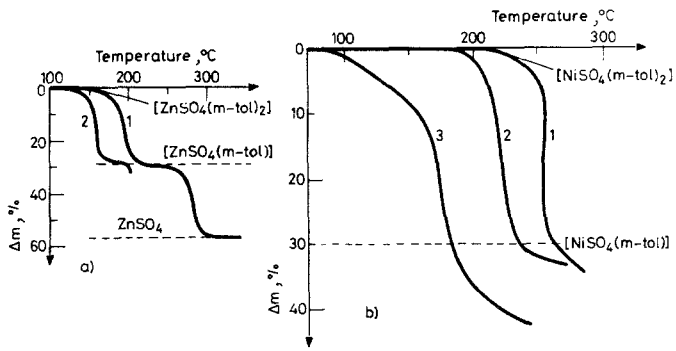

Fig. 5 Thermal dissociation of the complexes $[ZnSO_4(m\text{-tol})_2]$ (a) and $[NiSO_4(m\text{-tol})_2]$ (b). Sample holder: snap-lid crucible (1), open crucible (2) and plate holder (3). Heating program: quasi-isothermal; sample mass: 100 mg; atmosphere: helium

(iv) An intermediate phase exists; it is thermodynamically stable; at low pressures of the gaseous reaction product the kinetic stabilities of the initial phase and the internediate phase are close to one another

The thermal dissociation is a multistage process, with non-separated stages.

We studied the dehydration of EDTA complexes with the compositions $Mg_2L \cdot 9\ H_2O$ and $MgMnL \cdot 9\ H_2O$. These compounds contain two independent coordination spheres, with the water molecules occupying three different positions: $[Mg(H_2O)_6][MgL(H_2O)] \cdot 2\ H_2O$ and $[Mg(H_2O)_6][MnL(H_2O)] \cdot 2\ H_2O$ [3].

Study of the dehydration of the chelates under quasi-equilibrium conditions demonstrated the existence of the intermediate phases $Mg_2L \cdot 4\ H_2O$ and

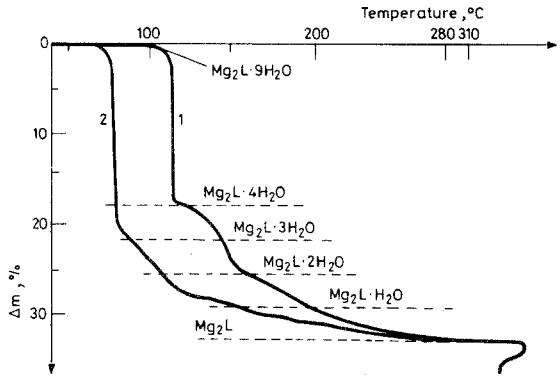

Fig. 6 Dehydration of the EDTA chelate $Mg_2L \cdot 9\,H_2O$ [16]. Sample holder: labyrinth holder (1), plate holder (2). Heating program: quasi-isothermal; sample mass: 250 mg, atmosphere: air

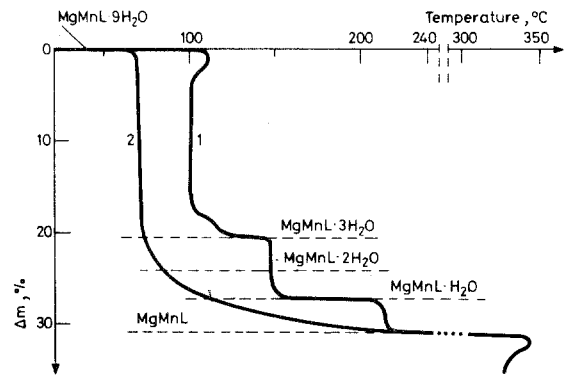

Fig. 7 Dehydration of the EDTA chelate $MgMnL \cdot 9\,H_2O$ [16]. Sample holder: labyrinth holder (1), plate holder (2). Heating program: quasi-isothermal; sample mass: 250 mg; atmosphere: air

$Mg_2L \cdot 2\,H_2O$, possessing poor stability even at $p_{H_2O} = 1$ atm. The intermediate phases $MgMnL \cdot 3\,H_2O$ and $MgMnL \cdot H_2O$ are more stable. When the water vapour pressure is reduced to $p_{H_2O} = 0.01$ atm, all the listed phases are thermodynamically unstable, and under quasi-equilibrium conditions they are formed only in insignificant amounts (Figs 6 and 7 [16]). It is possible, however, that these phases are kinetically sufficiently stable to accumulate in the course of the non-isothermal experiment. We did not attempt to separate them as independent phases, but utilized DTA and DDTA techniques (Figs 8 and 9). Both DTA curves of chelate dehydration are fairly "smooth"; however, the DDTA curves differ considerably. For the chelate $MgMnL \cdot 9\,H_2O$ the curve has only two maxima, corresponding to two inflexions in the DTA curve; the DDTA curve for the chelate $Mg_2L \cdot 9\,H_2O$ has a much more intricate appearance and clearly indicates a multistage process with non-separated stages.

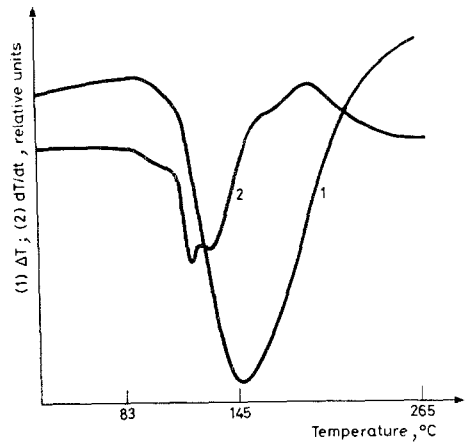

Fig. 8 Dehydration of the EDTA chelate $Mg_2L \cdot 9\ H_2O$. 1, DTA curve; 2, DDTA curve. Instrument: thermoanalyzer manufactured by Netzsch. Sample mass: 200 mg; atmosphere: nitrogen

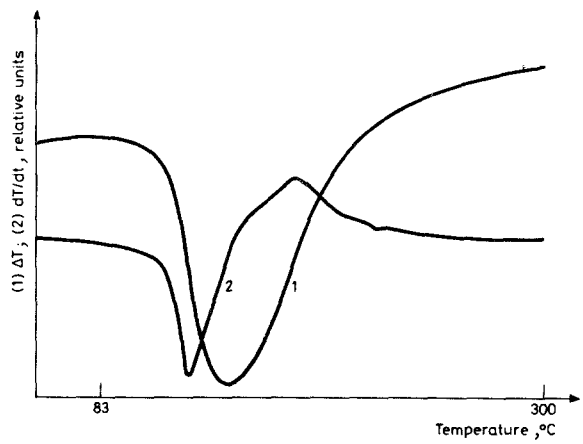

Fig. 9 Dehydration of the EDTA chelate $MgMnL \cdot 9\ H_2O$. 1, DTA curve; 2, DDTA curve. Instrument: thermoanalyzer manufactured by Netzsch. Sample mass: 200 mg; atmosphere: nitrogen

The dehydration kinetics of the chelate $Mg_2L \cdot 9\ H_2O$ cannot be studied in a manner such that the stages are separated, since the nonahydrate, tetrahydrate and dihydrate phases are close to one another in kinetic stability, and their decompositions proceed at similar rates in a given temperature interval. A simple calculation of the kinetic parameters by making use of overall kinetic curves (TG, DTA and EDG) is impossible.

Conclusions

The four cases discussed do not, of course, cover all possible varieties of multistep and multistage reactions in the thermal dissociation of compounds. However, their investigation indicates the necessity of analyzing the potential existence of several stages in such processes. This analysis should precede the final calculation of the kinetic constants via the relevant topochemical equation.

The general procedure for the ideal case should consist of the following steps:

(i) Thermogravimetry under quasi-equilibrium conditions (Q-derivatograph, four types of sample holders, $p_{gas} = 0.01-1$ atm).

(ii) Thermogravimetry with linear temperature increase, and simultaneous recording of DTA and DTG curves.

These two experiments will reveal the stoichiometry of the process, and the compositions of the theoretically possible thermodynamically stable and metastable phases.

(iii) Study of the process by DDTA or some analogous technique, and by modified DTG [17], which may yield important information on the non-separation of stages.

(iv) Synthesis (in particular, utilizing the decomposition processes in the Q-derivatograph) of relevant intermediate phases, in order to determine their kinetic stabilities.

(v) Study of the thermal dissociation under linear heating and far from the equilibrium state, in particular, by the EGD technique, in an inert gas flow through the sample ($m \leqslant 10$ mg, narrow fraction of large particles of the substance). These data can be used for kinetic calculations.

The rather cumbersome layout of the experimental steps as described above is due to the condition that in studies of heterogeneous thermal dissociation reactions of the type $A_s \rightarrow B_s + C_g$ one cannot change the concentrations of the reactants as in homogeneous systems, and hence the position of the equilibrium in the system is fully defined by the pressure of the evolved gas.

For this reason, thermal analysis under quasi-equilibrium conditions (Q-derivatograph) must be the first stage in any serious, correct and significant investigation concerning the kinetics of reversible thermal dissociation processes of compounds.

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Zusammenfassung — Die Untersuchung der Kinetik von über viele Schritte verlaufenden thermischen Dissoziationsreaktionen ist ein schwieriges Unterfangen. Mittels Thermogravimetrie unter Quasi-Gleichgewichtsbedingungen können intermediäre Phasen bestimmt und — falls notwendig — abgetrennt werden, um die kinetische Stabilität gesondert zu bestimmen. Parallele Anwendung der linearen nicht-isothermen und der quasi-isothermen Thermogravimetrie ermöglicht den Nachweis von metastabilen intermediären Phasen.

Резюме — Стадийность реакций термической диссоциации может существенно осложнить изучение кинетики этих процессов. Использование термогравиметрии в квази-равновесных условиях дает возможность определить промежуточные фазы и, в случае необходимости, выделить их для отдельного изучения кинетической устойчивости. Параллелное использование техники термогравиметрии при линейном нагреве и квази-равновесной термогравиметрии позволяет обнаружить существование промежуточной метастабильной фазы.