

CRTA FOR THE THERMOANALYTICAL SCREENING OF VOLATILE COMPOUNDS

3. Study on thermal destruction process, taking place simultaneously with evaporation process

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Abstract

Quasi-equilibrium thermogravimetry (variant of CRTA) is put to use as an express method of thermoanalytical screening for volatile compounds. During the experiments for P - T relationship calculations (running with several calibrated standard sample holders) the non-volatile (polymerized) residue is formed (and is decomposed with further temperature rising). Thermogravimetric data are used for the calculation of the kinetic parameters for the polymerization reaction, taking place (concurrently with the evaporation) in the melt of the studied volatile compound.

Keywords: coordination compounds, CRTA, kinetics, polymerization, pyrolysis, quasi-equilibrium, TG, thermolysis, volatility

Introduction

It is known that such volatile coordination compounds as acetylacetonates of different metals usually do not evaporate fully under heating. The residue is not volatile and decomposes during the pyrolysis process at high temperatures. Such a residue is perceived to be the result of the polymerization process with the stitching together of monomer molecules. The problem of the polymerization of β -diketonates in solid state, solutions, melts has not been adequately investigated, and these data are important for the understanding of the volatility and thermal stability of β -diketonates.

Quasi-equilibrium thermogravimetry [1-2] is the unique method for the study of any mass loss processes with good reversibility, such as thermal dissociation of coordination compounds (with neutral molecules as ligands), inclusion compounds (of very different types) [3] and sublimation and evaporation processes.

Quasi-equilibrium thermogravimetry is rather handy method for the fast study of metal β -diketonates' volatility, which are stable in air; it gives direct P - T relationship, even if as a rough approximation [4-5]. The commonly used sample holders (plate-like, open crucible, crucible with lid and conical) must be calibrated previously upon the vapor pressure. This calibration is effected by experiments with well characterized volatile substances (with known P - T relationship for sublimation and/or

evaporation), but only with big enough molecular masses M ($M \geq 250 \text{ g mol}^{-1}$, so as for such M the partial vapor pressure in the sample holder no longer depends on the coefficients of gases mutual diffusion) [4]. The decomposition rate 0.3 mg min^{-1} is quite enough for the sharp stabilization of the sublimation (evaporation) temperature during one or two hours of the experiment (with the reproducibility $\pm 3^\circ\text{C}$ from one run to another). It turns out that for the above listed set of sample holders (and such heavy organic molecules) the vapor partial pressure falls within the range between 0.0006 and 0.11 bar ($\pm 10\%$), which is distinct from the obtained gas partial pressure for dehydration or decarbonation processes (0.01–0.8 bar) with very small molecules of H_2O and CO_2 (and with big mutual diffusion coefficients in the ‘air–gas’ system).

Experimental and discussion

The acetylacetonate of chromium $\text{Cr}(\text{AA})_3$ ($M=350 \text{ g mol}^{-1}$) was chosen as a good model substance. It was synthesized by known method and purified by sublimation in vacuum.

Figure 1 shows TG-curves of the evaporation (Derivatograph Q-1500-D, sample mass 45 mg, TG sensitivity 50 mg, atmosphere: air, real experimental evaporation rate 0.3 mg min^{-1}) [4] in three different sample holders. From this Fig. 1 we notice that the greater the vapor partial pressure, the greater is the evaporation temperature. The greater the evaporation temperature, the smaller is the evaporated substance mass, so as the polymerization rate is larger at higher temperatures (whereas the evaporation rate is constant for all experiments). It is possible to calculate the accumulated non-volatile residue at every temperature and to calculate the rate of the residue formation (Table 1). While calculating this rate, we took into account the continuous decrease of the evaporating (and polymerizing) mass of the sample, which made us to double the polymerization rate.

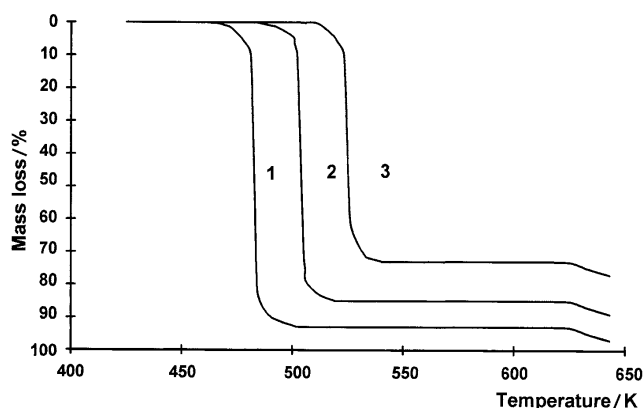


Fig. 1 Thermoanalytical curves for $\text{Cr}(\text{AA})_3$ under quasi-equilibrium conditions ($m=45 \text{ mg}$, $q=0.3 \text{ mg min}^{-1}$); sample holders: 1 – open crucible, 2 – crucible with lid, 3 – conical crucible

We exclude from consideration the time of linear heating before the stabilization of the temperature, believing that the introduced error counts very little in the calculations. Partially the pre-heating proceeds before the melting temperature (an estimated rate of polymerization in solid state is one order of magnitude smaller than in the melt) whereas the ensuing linear warming-up period of the melt is not long.

Table 1 Experimental and calculated data on the residue formation during the evaporation of $\text{Cr}(\text{AA})_3$ (starting sample mass 45 mg)

Sample holder	Quasi-equilibrium temperature/K	Residue/mg	Estimated time of evaporation/s	Polymerization rate/mol s ⁻¹
Open crucible	483±8	3.15	8370	2.16·10 ⁻⁹
Crucible with lid	503±3	6.75	7650	5.06·10 ⁻⁹
Conical holder	524	12.15	6570	10.60·10 ⁻⁹

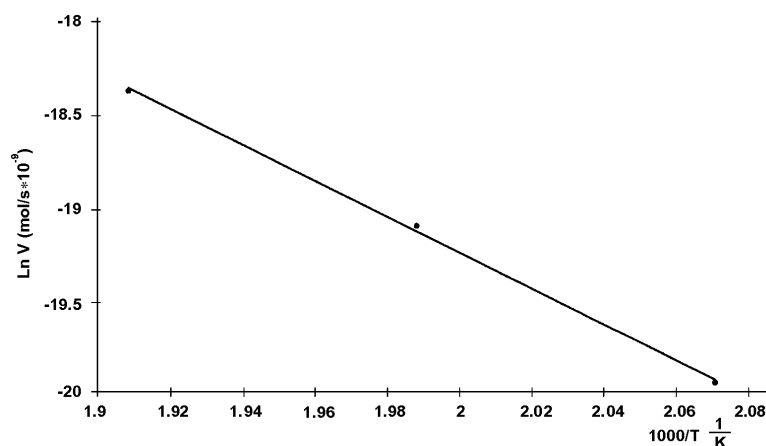


Fig. 2 Plot $\ln V$ vs. $1000/T$ for the calculation of activation energy E_a

The data from Table 1 was used for the calculation of the activation energy for polymerization process (Fig. 2). $E_a=81.5 \text{ kJ mol}^{-1}$.

Conclusions

Earlier we studied the thermal characteristics (volatility and thermal stability) of β -diketonates of lanthanides (*tris*-chelates: anhydrous LnL_3 and hydrated $\text{LnL}_3 \cdot n\text{H}_2\text{O}$ and anhydrous *tetrakis*-chelates: $\text{Na}[\text{LnL}_4]$ with branched and fluorinated ligands (dipivaloylmethane–DPM, trifluoroacetylacetone–TFA, hexafluoroacetylacetone–HFA, pivaloyltrifluoroacetone–PTA, dimethylheptafluoroacetone-dione–FOD) [6]. The non-volatile residue fell within the range between 3 and 35%, with high residue (10–35%) for hydrated compounds and low residue (3–10%) for anhydrous ones. We believed that the formation of the non-volatile residue for hydrates was connected with process of hydrolysis, such as:



The newly formed hydroxo-complexes are thermally unstable and readily polymerize, liberating gaseous product and leaving high percentage of non-volatile residue.

The formation of the non-volatile residue for anhydrous chelates can be connected with other route of polymerization.

It is agreed that the chelate $\text{Cr}(\text{AA})_3$ is very stable; the polymerization of this compound can be explained by the long period of heating of the melt in the presence of air. We cannot propose now the possible mechanism of the process. It is worth to note that the high stability of the sublimation temperature is the clear evidence of the absence of any non-equilibrium process of other gas evolution (owing to certain pyrolysis process).

Quasi-equilibrium thermogravimetry gives the rare possibility to study the evaporation and polymerization processes for volatile compounds simultaneously and independently of one another: stabilized temperatures of the sublimation in different sample holders allow to obtain $P-T$ relationship; different rates of the accumulation of the non-volatile residue in these conditions allow to calculate kinetic parameters of the polymerization.

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