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CRTA FOR THE THERMOANALYTICAL SCREENING OF VOLATILE COMPOUNDS

2. The volatility of trifluoroacetylacetonates of Al, Cr and Zr studied by the method of quasi-equilibrium thermogravimetry

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Abstract

Quasi-equilibrium thermogravimetry (with sample holders specially calibrated for the vapour pressure) was used for thermoanalytical screening of volatile compounds. 'p–T' relationships (in the range 0.0006 to 0.11 at) were obtained for acetylacetonates and fluoroacetylacetonates of Al, Cr and Zr. The incorporation of the trifluoromethyl group into the acetylacetone ligand noticeably increases the volatility: the enthalpy of evaporation remains practically constant, but the evaporation entropy changes distinctly.

Keywords: coordination compounds, CRTA, TG, quasi-equilibrium, thermodynamics, volatility

Introduction

Volatile coordination compounds are widely used in modern technologies of film deposition (MO CVD). Extensive research on the synthesis of such coordination compounds with different organic ligands (β-diketonates, etc.) is in proggress; it is well known that substitution of the radicals in the ligands and transformation to fluorinated derivatives changes noticeably the volatility and thermal stability of the substance. Thermoanalytical investigations are needed for the comparison of the volatilities of a series of such compounds.

We have demonstrated that quasi-equilibrium thermogravimetry can be used for this purpose [1–2]. It is clear from the mathematical relationship describing the phenomena that during sublimation (evaporation) of a compound the partial pressure of vapour in a sample holder depends on the product of two values: the molecular mass (M) of the vapour, and the coefficient of mutual diffusion (D) [2–3].

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We considered literature data available for molecular masses and coefficients of mutual diffusion. With increasing molecular mass the coefficient of mutual diffusion for the 'vapour air' system decreases. The value of the (M*D) product increases rapidly at average values of M and becomes practically constant at large values of M. At M>250 the value of the quasi-equilibrium partial pressure of the evolved vapour, p_0, will not depend on the nature of the compound [3].

Therefore, first the sample holder used must be calibrated against the partial pressure of well characterized volatile compounds (with known relationship $\ln p = B - A/T$), under conditions of quasi-isobaric quasi-isothermal heating. For this calibration it is possible to use any volatile compound with molecular mass M>250 g mol^{-1} [1–2]. Thereafter, in studies of new volatile compounds, the experimental data (stabilized equilibrium temperature of sublimation or evaporation at known partial vapour pressure in calibrated sample holders) allow plotting the 'p–T' relationship [1–2]. Although this relationship is not very precise, it is more informative for the strict comparison of the volatilities of compounds than the traditional set of thermal curves (TG, DTG, DTA *vs.* T) obtained with linear heating, because of their kinetic dependence.

In this work we have studied, using this method, the volatilities of several coordination compounds with organic ligands, for the demonstration of the influence of ligand exchange (of acetylacetone by trifluoroacetylacetone) on the volatility of the compounds.

Experimental

Trifluoroacetylacetonates of aluminium, chromium and zirconium were studied. They were synthesized by original methods [4] and purified by sublimation in vacuum.

Studies of the sublimation and evaporation of trifuoroacetylacetonates were conducted by means of a derivatograph Q-1500-D (MOM, Hungary). Four types of sample holder (preliminarily calibrated) [2] were used: multiplate sample holder (p_0= 0.0006±0.0002 at), open standard crucible (p_0= 0.009±0.002 at), crucible with lid (p_0= 0.022 ±0.002 at) and conical (p_0= 0.11±0.02 at) [2].

Sample mass 100 mg, TG sensitivity 50 and 100 mg, real experimental mass loss 0.3 mg min^{-1}, initial voltage 50 or 60 V, chart velocity 0.1 cm min^{-1}. For checking the constancy of the mass loss rate we recorded TG and T curves *vs.* the time, although simple recording TG *vs.* T was used also. The temperature of evaporation (sublimation) became stable only after 80–100 min of heating and was constant (±1 K) during 150–200 min. Usually 80–93% of the compound was evaporated, the residue (maybe a polymerized substance) was decomposed with further temperature rise.

Experimental data on the volatility of Al- and Cr-acetylacetonates were taken from [2].

Results and discussion

Table 1 lists the experimental temperatures of quasi-equilibrium evaporation for the studied complexes. Figure 1 shows 'p–T' relationships, constructed for the studied compounds on the basis of these temperatures and known partial vapour pressures, maintained in the sample holders used [1].

Three experimental points (open crucible, crucible with lid and conical holder) were quite enough for the evaluation of the 'liquid – vapour' equilibrium of evaporation. Low-temperature sublimation process was observed for the ma-

Table 1 Experimental data on the volatility of the investigated compounds

Compound	Stabilized temperature/K			
	Evaporation			Sublimation
	conical crucible	crucible with lid	open crucible	multiplate sample holder
$Al(AA)_3$[2]	516±4*	475±3*	457±4*	408
$Al(TFA)_3$	473	445	423	389
$Cr(AA)_3$[2]	524	503±3*	483±8*	446
$Cr(TFA)_3$	487	466	453	408
$Zr(AA)_4$	–	–	–	444**
$Zr(TFA)_4$	–	451±2*	438±2*	395±1*

*- the average from 5 experiments,
**- calculated from the data in [4].

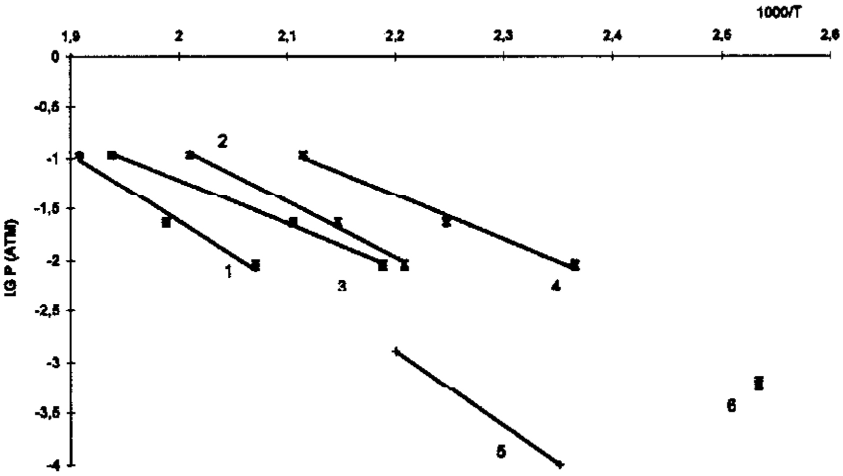

Fig. 1 'p–T' relationships for the investigated compounds. Evaporation: 1 – $Cr(AA)_3$, 2 – $Cr(TFA)_3$, 3 – $Al(AA)_3$, 4 – $Al(TFA)_3$
Sublimation: 5 – $Zr(AA)_4$ (extrapolation from [4]), 6 – $Zr(TFA)_4$

jority of the compounds studied only in the multiplate sample holder; we can obtain only one 'p–T' point for the 'solid – vapour' equilibrium (Fig. 1).

As is clear from the picture, the incorporation of the trifluoromethyl-group into the β-diketone ligand increases the volatility of the compounds; the enthalpy of evaporation does not change noticeably, but the evaporation entropy changes distinctly. The increase in volatility (after ligand fluorination) is common for this class of compounds [5–6], but the importance of enthalpy or entropy contribution has not been specially considered.

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