

## **DSC AND VAPOUR PRESSURE INVESTIGATION OF SOME $\beta$ -DIKETONATES**

*V. B. Lazarev, J. H. Greenberg, Z. P. Ozerova and G. A. Sharpataya*

KURNAKOV INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY,  
ACADEMY OF SCIENCES, 117907 MOSCOW, LENINSKII PROSP. 31, U.S.S.R.

DSC and vapour pressure measurements are presented on some Be, Al and Cr complexes with 2,4-pentanedione tetramethyl-3,5-heptanedione, 1,1,1-trifluoro-2,4-pentanedione and hexafluoro-2,4-pentanedione. Thermodynamic functions are given for the sublimation, vaporization and melting processes of the substances.

Chelate complexes of different metals with a number of  $\beta$ -diketones are used in analytical chemistry, in refining and separation process, and for the preparation of thin films. Recently, an interesting application was found for Be complexes in Li-Be gas-phase neutrino detectors. To optimize all these **technologies**, the thermodynamic properties of both the condensed and the gaseous complexes should be available. In the present communication, results are discussed concerning the thermodynamics of melting and evaporation of some Be, Al and Cr complexes with the following  $\beta$ -diketones: 2,4-pentanedione (HAA), tetramethyl-3,5-heptanedione (HTHD), 1,1,1-trifluoro-2,4-pentanedione (HATA) and hexafluoro-2,4-pentanedione (HHFA).

All the substances were prepared by conventional chemical techniques, from a soluble salt and the corresponding  $\beta$ -diketone.  $\text{Al}(\text{AA})_3$  and  $\text{Cr}(\text{AA})_3$  were also prepared by means of an electrochemical method [1]. In the latter, a glass electrolyzer was used with a magnetic mixer and two electrodes: a platinum cathode and the corresponding metal anode. The electrolyte was a 30% solution of the ligand in acetonitrile containing 0.1 M  $\text{Bu}_4\text{NFB}_4$ . After 3-4 Ah of electricity had passed through the solution, it was treated with an ether + acetone (5 : 1) mixture. The resulting precipitate was filtered off and dried in vacuum. The final yield was 92% for  $\text{Al}(\text{AA})_3$  and 91% for  $\text{Cr}(\text{AA})_3$ .

The substances were identified via chemical analysis and IR spectra. The samples used for thermodynamic investigations were subsequently sublimed twice in vacuum in a temperature gradient. The experimental results obtained proved to be independent of the preparation method.

Melting temperatures and enthalpies were measured with Mettler TA-3000 and SETARAM DCS 111 differential scanning calorimeters, respectively. Impurity concentrations in  $\text{Al}(\text{AA})_3$  and  $\text{Be}(\text{ATA})_2$  were below the limits detectable with the calorimeters, while  $\text{Cr}(\text{AA})_3$  and  $\text{Be}(\text{AA})_2$  were 99.9% pure.

The total vapour pressure was measured with a silica Bourdon gauge in conjunction with a standard mercury manometer. The vapour pressure apparatus and the measuring procedure have been described elsewhere [2]. The vapour compositions were analysed via unsaturated vapour pressure measurements. It was shown from both the sublimation and the vaporization of all the substances (except  $\text{Be}(\text{HFA})_2$ ) that only monomeric gaseous molecules were formed. This means that melting is also a congruent process.  $\text{Be}(\text{HFA})_2$  was found to decompose long before melting.

Experimental results and derived thermodynamic functions are summarized in the following Table.

Table 1

Compound	Process	T, K	$\lg P(\text{Pa}) = A - B/T$		$\Delta H_T^0$ , kJ mol <sup>-1</sup>	$\Delta S_T^0$ , J mol <sup>-1</sup> deg <sup>-1</sup>
			A	B		
$\text{Be}(\text{AA})_2$	I	380.3 ± 0.2	—	—	13.8 ± 0.1	36.3 ± 0.4
	II	—	13.625	4300	82.3	165.0
	III	382–511	11.260	3400	65.7 ± 1.0	119.7 ± 2.2
$\text{Be}(\text{THD})_2$	I	368.1 ± 0.2	—	—	20.0 ± 0.1	54.3 ± 0.4
	II	—	13.765	4400	84.2	167.8
	III	383–525	10.935	3400	65.1	113.5 ± 1.4
$\text{Be}(\text{ATA})_2$	I	384.4 ± 0.2	—	—	26.7 ± 0.2	69.4 ± 0.8
	II	354–383	14.645	4460	85.3 ± 6.3	184.5 ± 8.7
	III	387–474	11.214	3120	59.8 ± 0.4	118.9 ± 1.1
$\text{Be}(\text{HFA})_2$	I	355.4 ± 0.2	—	—	—	—
	II	289–349	14.715	3450	—	—
$\text{Al}(\text{AA})_3$	I	466.7 ± 0.2	—	—	33.7 ± 0.3	72.1 ± 0.6
	II	432–464	14.550	5300	102.0 ± 3.2	182.7 ± 7.6
	III	468–515	11.981	4100	78.7 ± 0.9	133.6 ± 1.9
$\text{Al}(\text{HFA})_3$	I	346.2 ± 0.2	—	—	35.1 ± 0.3	101.4 ± 1.0
	II	324–344	14.604	4060	77.6 ± 6.2	183.8 ± 9.3
	III	349–411	11.761	3070	58.7 ± 0.7	129.3 ± 1.9
$\text{Cr}(\text{AA})_3$	I	488.9 ± 0.5	—	—	34.0 ± 0.3	69.5 ± 0.2
	II	357–486	15.179	5900	113.0 ± 4.8	194.8 ± 10.2
	III	490–536	11.981	4300	82.2 ± 2.0	131.8 ± 4.0

I – melting, II – sublimation, III – vaporization

## References

- 1 J. H. Greenberg, V. B. Lazarev, A. J. Zavernjaev, V. A. Shreider and S. D. Chepik, Zh. Fizicheskoi Khimii, 60 (1986) 1044.
- 2 J. H. Greenberg, V. B. Lazarev, A. J. Zavernjaev, V. A. Shreider and S. D. Chepik, Zh. Fizicheskoi Khimii, 60 (1986) 1386.

**Zusammenfassung** — Die Ergebnisse von DSC- und Dampfdruckmessungen einiger Komplexe von Beryllium, Aluminium und Chrom mit 2,4-Pentandion (HAA), Tetramethyl-3,5-heptandion (HTHD), 1,1,1-Trifluoro-2,4-pentandion (HATA) und Hexafluoro-2,4-pentandion (HHFA) werden beschrieben. Die berechneten thermodynamischen Funktionen für Sublimation, Verdampfung und Schmelzen der Komplexverbindungen sind tabelliert.

**Резюме** — Представлены ДСК данные и измерения давления пара для комплексов бериллия, алюминия и хрома с 2,4-пентандионом, 1,1,1-трифтор- и гексафтор-2,4-пентандионом и тетраметил-3,5-пентандионом. Приведены термодинамические функции для процессов сублимации, испарения и плавления этих комплексов.