# Vapour pressures and standard molar enthalpy of sublimation of crystalline tris(pentane-2,4-dionato)ruthenium(III)

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## Abstract

The Knudsen mass loss effusion technique was used to measure the vapour pressure of crystalline tris(pentane-2,4-dionato)ruthenium(III) as a function of temperature between 398.18 and 413.15 K using three different effusion holes. From the temperature dependence of the vapour pressure, the standard molar enthalpy of sublimation at the mean temperature of the experimental temperature range, 405.7 K, was derived as $139.7 \pm 2.5$ kJ mol$^{-1}$. Using an estimated value of $\Delta_{cr}^{g} C_{p}^{o} = -50$ J K$^{-1}$ mol$^{-1}$, the standard molar enthalpy of sublimation at 298.15 K was calculated as $145.1 \pm 2.5$ kJ mol$^{-1}$.

## 1. Introduction

A large amount of work has been done on the thermochemistry of metal-$\beta$-diketonates, as can be seen in some recent review articles [1, 2]. However, no thermochemical studies have been reported for the complexes of $\beta$-diketones with ruthenium(III). Here we report results for the vapour pressures and standard molar enthalpy of sublimation of crystalline tris(pentane-2,4-dionato)ruthenium(III).

## 2. Experimental details

Tris(pentane-2,4-dionato)ruthenium(III), Ru(ACAC)$_3$, was prepared according to a literature method [3] by mixing an aqueous solution of RuCl$_3$ with an ethanolic solution of 2,4-pentanedione with K$_2$CO$_3$ and then refluxing the mixture. The complex was extracted with benzene and purified by crystallization from benzene and then by repeated sublimation *in vacuo*. Its melting point is 260 °C (decomposes).

The vapour pressure as a function of temperature was measured using our mass loss Knudsen effusion apparatus. The detailed description of the apparatus, procedure and technique and the results obtained with test substances (benzoic acid and ferrocene) have already been reported [4]. This apparatus enables the simultaneous operation of three Knudsen cells with three different holes.

In each effusion experiment the mass loss $\Delta m$ of the crystalline sample was measured by weighing the cell (containing the sample) to $\pm 0.01$ mg before and after a convenient effusion time period $t$ in a system evacuated to near $1 \times 10^{-4}$ Pa. The cells were immersed in a thermostatically controlled silicone oil bath. At the temperature $T$ of the experiment the vapour pressure $p$ was calculated from

$$p = \frac{\Delta m}{A_o w_o t} \left( \frac{2 \pi R T}{M} \right)^{1/2} \tag{1}$$

in which $A_o$ is the area of the effusion hole, $w_o$ is the corresponding Clausing factor, $w_o = [1 + (3l/8r)]^{-1}$,

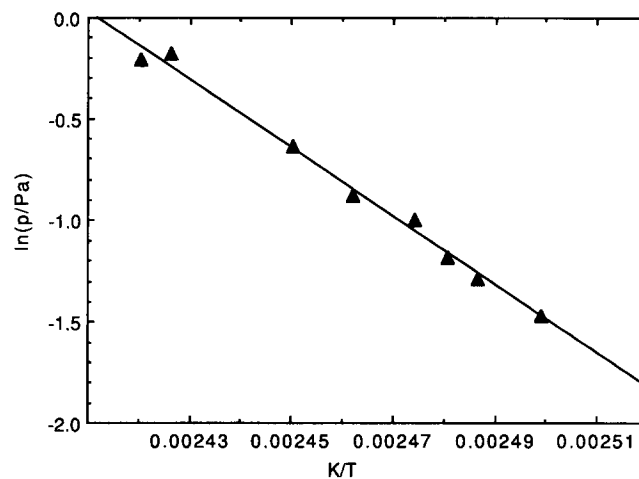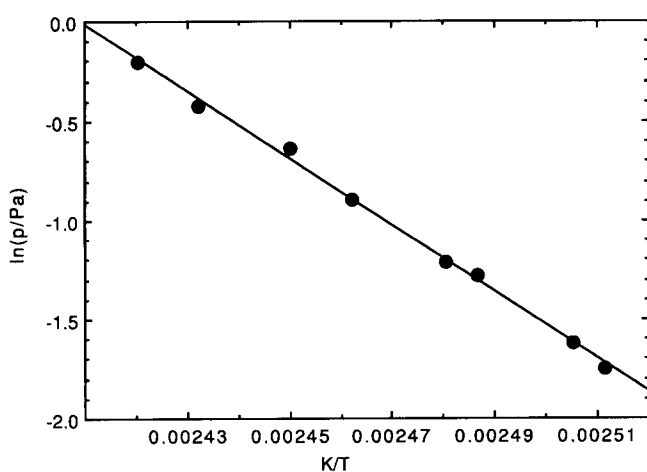TABLE 1. Experimental results and residuals of Clausius–Clapeyron equation

| $T$ (K) | $p$ (Pa) | | | $100\Delta(\ln p)$ | | |
|---|---|---|---|---|---|---|
| | Hole 1 | Hole 2 | Hole 3 | Hole 1 | Hole 2 | Hole 3 |
| 398.18 | | 0.1733 | | | −2.76 | |
| 399.17 | 0.2083 | 0.1978 | | −4.62 | −0.01 | |
| 400.15 | 0.2551 | | 0.2308 | 5.34 | | 0.41 |
| 402.15 | 0.2752 | 0.2769 | 0.2765 | −7.93 | 2.40 | −2.40 |
| 403.13 | 0.3382 | 0.2972 | 0.3061 | 2.54 | 0.30 | −2.42 |
| 404.16 | 0.3915 | | 0.3692 | 6.60 | | 5.70 |
| 406.15 | 0.4678 | 0.4088 | 0.4172 | 4.01 | 0.15 | −2.47 |
| 408.13 | 0.5203 | 0.5284 | 0.5285 | −5.31 | 5.72 | 1.07 |
| 410.13 | 0.6694 | | | −0.16 | | |
| 411.14 | 0.7141 | 0.6518 | | −3.75 | −3.47 | |
| 412.15 | 0.8544 | | 0.8331 | 4.20 | | 6.37 |
| 413.15 | 0.8952 | 0.8126 | 0.8106 | −0.98 | −1.33 | −6.24 |

TABLE 2. Parameters of Clausius–Clapeyron equation and standard enthalpies of sublimation

| Hole | $a$ | $b$ | $T_m$ (K) | $\Delta_{cr}^g H_m^\circ(T_m)$ (kJ mol$^{-1}$) | $\Delta_{cr}^g H_m^\circ$ (298.15 K) (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 1 | $40.48 \pm 1.35$ | $16767 \pm 547$ | | $139.4 \pm 4.5$ | |
| 2 | $40.52 \pm 0.90$ | $16822 \pm 363$ | | $139.9 \pm 3.0$ | |
| 3 | $40.57 \pm 1.54$ | $16824 \pm 623$ | | $139.9 \pm 5.2$ | |
| Mean | $40.52 \pm 0.74$ | $16804 \pm 302$ | 405.66 | $139.7 \pm 2.5$ | $145.1 \pm 2.5$ |

TABLE 3. Values of $p$ and $T$ from the vapour pressure equation (mean values)

| $p$ (Pa) | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|---|---|---|---|---|---|---|---|---|
| $T$ (K) | 398.87 | 402.74 | 405.53 | 407.73 | 409.55 | 411.09 | 412.44 | 413.63 |
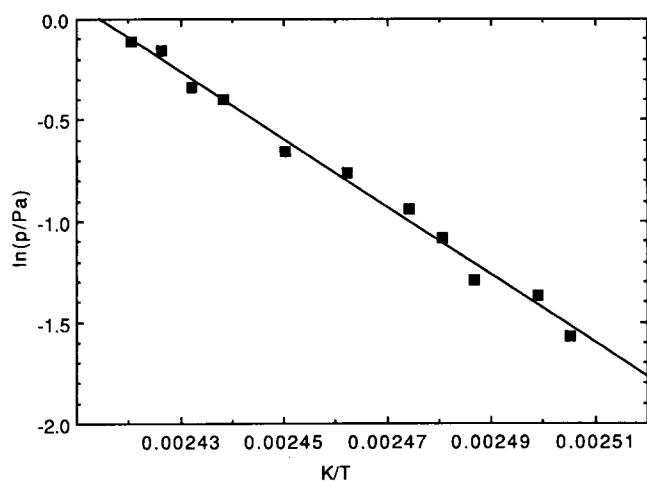


Fig. 1. Plot of $\ln p = f(1/T)$ for hole 1.



Fig. 3. Plot of $\ln p = f(1/T)$ for hole 3.



Fig. 2. Plot of $\ln p = f(1/T)$ for hole 2.

where $l$ is the thickness of the effusion holes and $r$ is the radius, $M$ is the molar mass of the effusing vapour and $R$ is the gas constant. The thickness of the effusion holes, $l$, was 0.049 mm and their areas and Clausing factors were as follows: hole 1 — $A_o = 0.596$ mm$^2$;

$w_o = 0.959$; hole 2 — $A_o = 0.813$ mm$^2$; $w_o = 0.965$; hole 3 — $A_o = 0.862$ mm$^2$; $w_o = 0.966$.

## 3. Results

The Clausius–Clapeyron equation $\ln p = a - b/T$, where $p$ is in pascals and $b = \Delta_{cr}^g H_m^\circ(T_m)/R$, was used to derive the standard molar enthalpies of sublimation at the mean temperature of the experimental temperature range, $\Delta_{cr}^g H_m^\circ(T_m)$. The calculated enthalpies of sublimation obtained from each individual hole are in agreement within experimental uncertainty.

The experimental results obtained from each cell together with the residuals of the Clausius–Clapeyron equations obtained from least-squares adjustment are given in Table 1. The plots of $\ln p = f(1/T)$ for the individual effusion holes used are presented in Figs. 1–3.

Table 2 presents for each hole the detailed parameters of the Clausius–Clapeyron equation and the mean temperature of the experiments, $T_m = 405.66$ K; the

mean values and the standard molar enthalpy of sublimation at 298.15 K, $\Delta_{cr}^{g}H_{m}^{o}$ (298.15 K), are also presented. This value was derived from the mean value of the sublimation enthalpy calculated at the mean temperature $T_{m}$ of the experiments by the equation

$\Delta_{cr}^{g}H_{m}^{o}$(298.15 K)

$$= \Delta_{cr}^{g}H_{m}^{o}(T_{m}) + \Delta_{cr}^{g}C_{p,\,m}^{o}(298.15\ K - T_{m}) \qquad (2)$$

Since there are no published values of $\Delta_{cr}^{g}C_{p,\,m}^{o}$ for the studied compound, we assumed $\Delta_{cr}^{g}C_{p,\,m}^{o} = -50$ J $K^{-1}$ mol$^{-1}$ in our calculations in accordance with estimations made by other authors [5], yielding the value $\Delta_{cr}^{g}H_{m}^{o}$(Ru(ACAC)$_3$, 298.15 K) = 145.1 ± 2.5 kJ mol$^{-1}$. Table 3 lists the values of $p$ and $T$ calculated from the $(p, T)$ equation derived from the global results within the experimental range of pressures used, 0.2–0.9 Pa.

## Acknowledgments

## References

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