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THERMODYNAMIC PROPERTIES OF BENZOYLFERROCENE AND 1,1′-DIBENZOYLFERROCENE *

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ABSTRACT

The vapor pressures of benzoylferrocene and 1,1′-dibenzoylferrocene were measured by torsion-effusion technique. The following pressure–temperature equations were derived

benzoylferrocene $\log P(\text{kPa}) = 10.75 \pm 0.22 - (5314 \pm 82)/T$

1,1′-dibenzoylferrocene $\log P(\text{kPa}) = 9.29 \pm 0.24 - (4898 \pm 91)/T$

Second-law treatment of the experimental data yielded the sublimation enthalpies for benzoylferrocene and 1,1′-dibenzoylferrocene: $\Delta H^0_{\text{sub},298} = 116.3 \pm 6.0$ kJ mole^{-1} and $\Delta H^0_{\text{sub},298} = 109.3 \pm 6.0$ kJ mole^{-1}, respectively. Thermal functions of these compounds were also estimated.

INTRODUCTION

As a further contribution to our ongoing program [1] concerning the thermodynamic characterization of ferrocene derivatives, in this study the vapor pressures of benzoylferrocene and 1,1′-dibenzoylferrocene were determined by torsion-effusion method. Interest in the ferrocene derivatives, not yet extensively investigated, arises from the necessity of a wider understanding of the influence of the substitutional groups on the heat capacities, vapor pressure and sublimation heats. In addition, the determination of these thermodynamic quantities is of great importance in the practical application of these ferrocene derivatives, as evidenced in recent studies on the application of ferrocene derivatives as thermostabilizers against degradation of polyethylene [2,3], flame resistant polyester resins, etc. (see ref. 1 and refs. therein).

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Experimental

Benzoylferrocene (BF) and 1,1′-dibenzoylferrocene (DBF) were prepared, as described previously [4], by adding a solution of benzoyl chloride and aluminium trichloride, in dry methylene chloride, to a solution of ferrocene in dry methylene chloride. Final purification of the products was performed by chromatographic method on alumina, employing benzene and ether as eluents. The purity of the compounds was checked by thin layer chromatography on alumina plates using benzene as eluent. The melting-points of the two compounds (111.0°C and 106.5°C for BF and DBF, respectively) were measured and compared with the theoretical values [5]. Elemental analysis for C and H was also performed. The data are reported in ref. 4.

The vaporization experiment of BF and DBF was carried out using the torsion-effusion technique. Details of the technique and the experimental apparatus have been reported previously [1,6,7]. The vapor pressure of the sample, at each temperature of the glass effusion cell, was derived from the torsion angle (α) of the tungsten wire from the relation

$$P = 2K\alpha(a_1b_1f_1 + a_2b_2f_2)^{-1} = K^0\alpha$$

The constant K^0, which takes into account the geometrical constants of the cell and the torsion constant of the tungsten fiber, was calibrated before and after the vapor pressure measurements of the two compounds by vaporizing standard mercury and ferrocene [1,8], each at several different temperatures.

The value $K^0 = (8.32 \pm 0.25)\ 10^{-5}$ kPa deg^{-1}, derived before the vaporization of BF and DBF did not change significantly. The temperature was measured using a calibrated thermometer inserted into the glass effusion cell, as shown previously [1]. The accuracy of the temperature readings was tested by determining the melting point of ferrocene using the experimental apparatus.

RESULTS AND DISCUSSION

The vapor pressure data obtained for BF and DBF are reported in Table 1 and plotted as $\log_{10}P$ vs. $1/T$ in fig. 1. Least-squares treatment of the data yielded the following pressure–temperature equations

$$\text{BF}\quad \log P\,(\text{kPa}) = 10.75 \pm 0.22 - (5314 \pm 82)/T \tag{1}$$

$$\text{DBF}\quad \log P\,(\text{kPa}) = 9.29 \pm 0.24 - (4898 \pm 91)/T \tag{2}$$

where the associated errors are the standard deviations.

From equations (1) and (2) $\Delta H^0_{\text{sub},370} = 101.7 \pm 1.6$ kJ mole^{-1} and $\Delta H^0_{\text{sub},370} = 93.8 \pm 2.1$ kJ mole^{-1} were derived for BF and DBF, respectively. Recent work [4] on the heat capacities of benzoylferrocene and 1,1′-dibenzoylferrocene allowed calculation of the enthalpic functions for the solid phase.

TABLE 1

Vapor pressure of benzoylferrocene and 1,1′-dibenzoylferrocene

BF			DBF		
T (K)	α (deg)	$P \times 10^5$ (kPa)	T (K)	α (deg)	$P \times 10^5$ (kPa)
358	1	8.32	358	0.5	4.16
366	2	16.62	366	1.0	8.32
371	3	25.93	371	1.5	12.46
373	4	33.23	378	2.5	20.77
376	5	41.64	381	3.5	29.08
378	6	49.95			
380	7	58.26			
382	8	66.57			

The heat content and free energy functions of the gas phase were evaluated through the usual equations of statistical thermodynamics. Since no molecular constants, geometrical parameters and vibrational fundamentals are available in the literature some assumptions were made:

(a) both these molecules were regarded as substituted ferrocenes;

(b) the bond lengths and angles were transferred from ferrocene [9] and similarly for the $CO(C_6H_5)$ [10];

(c) the $3n - 6$ frequencies were also transferred from ferrocene [11] and from the substituent [12].

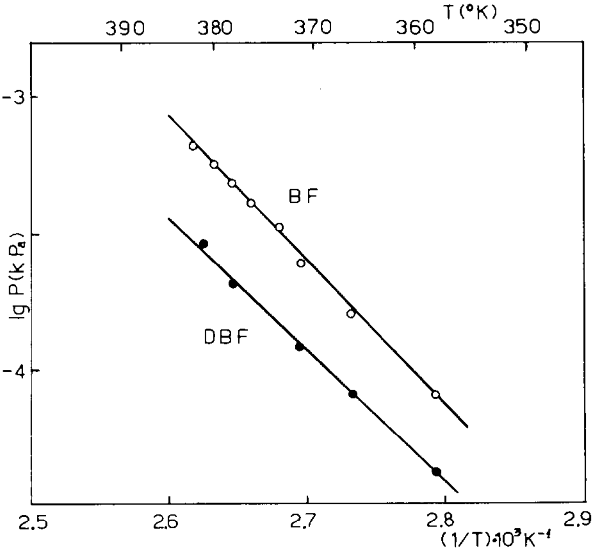

Fig. 1. Experimental vapor pressure of benzoylferrocene (BF) and 1,1′-dibenzoylferrocene (DBF).

TABLE 2

Thermodynamics functions of benzoylferrocene and 1,1'-dibenzoylferrocene

	Solid		Gas	
T (K)	$(H_T^0 - H_{298}^0)$ [a] (J mole^{-1})	$-(G_T^0 - H_{298}^0)/T$ (J mole^{-1} K^{-1})	$(H_T^0 - H_{298}^0)$ (J mole^{-1})	$-(G_T^0 - H_{298}^0)/T$ (J mole^{-1} K^{-1})
Benzoylferrocene				
298.15		272.1		483.0
350	23623	276.7	13899	486.1
360	28957	279.3	16870	487.3
370	34543	281.8	19933	488.7
380	40384	284.4	23083	490.2
390	46501	286.9	26322	491.9
	±500	±15.0	±1000	±10.0
1,1'-Dibenzoylferrocene				
298.15		327.0		513.1
350	28188	332.8	17523	517.0
360	34505	335.8	21288	518.6
370	41116	338.8	25179	520.3
380	48016	341.8	29192	522.3
390	55134	344.7	33326	524.3
	±500	±15.0	±1000	±10.0

[a] See ref. 4.

The thermal functions $[(G_T^0 - H_{298}^0)/T]_{\text{gas}}$ and $(H_T^0 - H_{298}^0)_{\text{gas}}$ are listed in Table 2. The associated uncertainties were determined taking into account that the molecular constants were estimated. The second-law sublimation enthalpies obtained for BF and DBF were $\Delta H_{\text{sub},298}^0 = 116.3 \pm 6.0$ kJ mole^{-1} and $\Delta H_{\text{sub},298}^0 = 109.3 \pm 6.0$ kJ mole^{-1}, respectively. The errors are an overall estimation of the relative uncertainties associated with the enthalpic function evaluation and the standard deviation of the experimental data.

The free energy functions for the solid phase were estimated by mean of the third-law equation

$$\left[\left(G_T^0 - H_{298}^0\right)/T\right]_{\text{sol}} = \left[\left(G_T^0 - H_{298}^0\right)/T\right]_{\text{gas}} + \left(\Delta H_{\text{sub},298}^0/T\right) + R \ln K_{\text{p}} \qquad (3)$$

and are listed in Table 2.

In this work the thermal functions of the gaseous phase were evaluated on the basis of structural and spectroscopic estimations. The reliability of these assumptions could be checked by deriving from our available data the $(S_{298}^0)_{\text{sol}}$ of the two compounds. The derivation was performed through the relation

$$\left(S^0_{298}\right)_{\text{sol}} = \frac{1}{T}\int_{298}^{T}\left(C_{\text{p}}\right)_{\text{sol}} \,\mathrm{d}T - \left[\frac{\left(G^0_T - H^0_{298}\right)}{T}\right]_{\text{sol}} - \int_{298}^{T}\frac{\left(C_{\text{p}}\right)_{\text{sol}}\,\mathrm{d}T}{T} \tag{4}$$

Values of $(S^0_{298})_{\text{sol}} = 272.1$ J mole^{-1} K^{-1} and 327.0 J mole^{-1} K^{-1} were obtained for BF and DBF, respectively. These values are comparatively higher than $(S^0_{298})_{\text{sol}} = 216.63$ J mole^{-1} K^{-1} obtained for ferrocene [13], as expected from the presence of massive bodies such as $CO(C_6H_5)$ in the derivatives investigated in this study. We feel that an uncertainty of 10% should be associated with these values.

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