Thermochimica Acta, 231 (1994) 333–335
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01393-H

Note

Thermal analyses and electrical studies of bis[dicarbonyl(π-cyclopentadienyl)iron(II)]

J.R. Allan * and A.D. Paton

Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh (UK)

(Received 8 June 1993; accepted 8 June 1993)

Abstract

The temperature-dependent conductivity measurements and thermal stability are studied for bis[dicarbonyl(π-cyclopentadienyl)iron(II)].

INTRODUCTION

Spectral and magnetic studies have shown that the compound $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ is diamagnetic, with an Fe–Fe bond, and has terminal and bridging carbonyl groups [1]. The compound exists in the trans form in the solid state; in solution both cis and trans forms can exist and behaviour is fluxional [1]. The present work was undertaken to ascertain the thermal stability of $[(h^5\text{-}C_5H_5)Fe(CO_2]_2$ and to obtain information about the electrical conductivity of the compound.

EXPERIMENTAL

Preparation of $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$

The compound was prepared by refluxing under nitrogen the uncracked cyclopentadiene dimer $(C_5H_6)_2$ with iron carbonyl, $Fe(CO)_5$, at 135–140°C for 8 h [1–3].

Thermal analysis

The thermal analysis studies were carried out using a Stanton Redcroft model STA 1500 thermobalance. Thermogravimetry and differential analysis curves were obtained at a heating rate of 6°C min^{-1} in static air.

Electrical measurements

The electrical measurements carried out on the prepared compound involved measuring the current as a function of voltage at room

* Corresponding author.

temperature to obtain the electrical conductivity σ of the compound. For such measurements, the compound was formed into a disc of diameter 13 mm and thickness approximately 1 mm, by compressing the powdered compound in a hydraulic press set to apply a force of 100 kN. The disc thickness was accurately measured by a micrometer. Circular electrodes of known diameter were formed concentrically on the flat faces of the disc by applying silver conductive paint through masks. The disc was then stored in a dessicator for several days before being tested.

The room-temperature dark current was measured for a series of applied d.c. voltages using a Keithley 610C electrometer. To test that the electrodes were ohmic and non-blocking, the voltage was increased in stages from zero to 30 V and then decreased in corresponding stages; this procedure was then repeated in reverse polarity. Agreement, within a maximum of ±10%, between the four readings of current was regarded as confirmation that the electrodes were not rectifying significantly.

Temperature-dependant conductivity measurements were obtained by placing the disc in an electrically heated oven over the approximate range 293–340 K. During the heating cycle, a constant potential of 10 V was applied across the disc whilst pairs of readings of current and temperature were obtained at frequent intervals. The latter readings used a calibrated copper–constantan thermocouple, formed from 44 SWG wires, having its hot and cold junctions on the disc and in melting ice, respectively.

DISCUSSION

The TG and DTA traces for $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$, Fig. 1, show that it is thermally stable in the range 20–130°C. At 130°C, the compound undergoes rapid pyrolytic decomposition to form a stable intermediate compound which could be isolated. From the DTA trace, it can be seen that this rapid

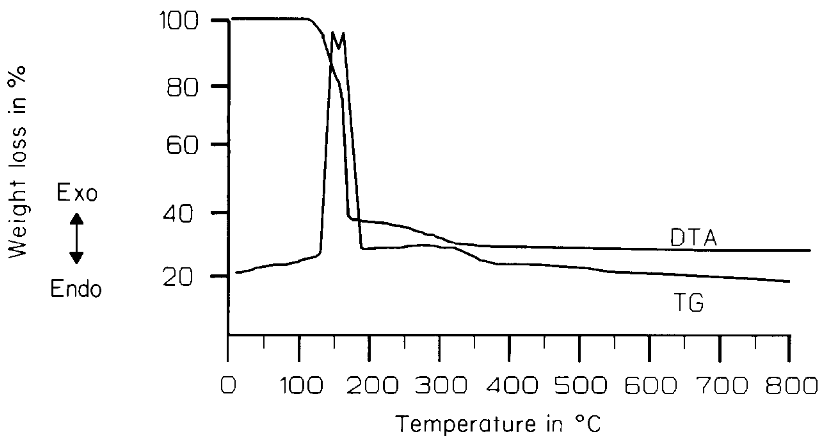

Fig. 1. TG and DTA trace for $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$.

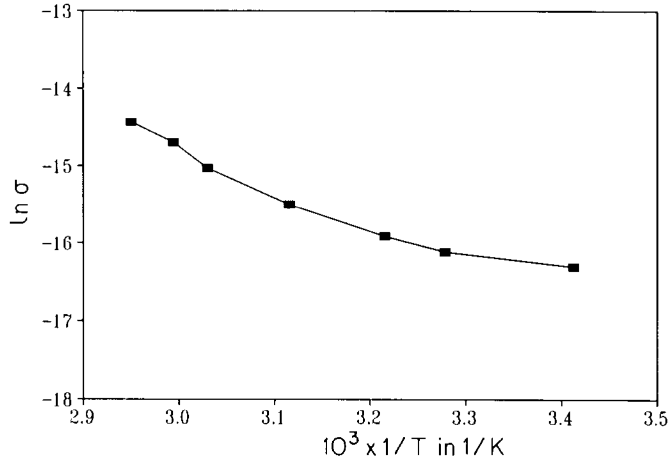

Fig. 2. Plot of ln σ versus $1000/T$ (where σ is conductivity in units of $\Omega^{-1}\,m^{-1}$ and T is the absolute temperature in K) for a disc of $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$.

pyrolysis is associated with a large exothermic reaction. Analysis of the stable intermediate compound showed it to have the empirical formula $FeC_2H_2O_6$. The intermediate compound begins slowly to decompose at 230°C and at 380°C, oxidation is complete and a residue of iron oxide remains.

The room-temperature current I versus voltage V characteristics were obtained under conditions of rising and falling voltage in both polarities. The current versus voltage relationship for $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ was observed to be linear throughout the voltage range investigated, indicating that ohmic electrical conduction prevailed. From the mean gradient of the I–V characteristics, the electrical conductivity for the compound was determined as $3.08 \times 10^{-8}\,\sigma^{-1}\,m^{-1}$.

The temperature dependence of the conductivity σ for $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ is shown in Fig. 2 as a plot of ln σ versus $1000/T$ where T is the absolute temperature. Linearity of such plots would show the validity of the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$, assuming the band model is applicable, where ΔE can be considered as the activation energy for releasing free carriers. Hence, from this equation a value of ΔE can be derived from the gradient of the Arrhenius plot. As shown in Fig. 2, the linearity of the plot is poor and caution must be exercised in attaching meaning to a ΔE value determined from this plot. From linear regression of the data of the Arrhenius plot, a ΔE value of 0.71 eV has been deduced for this compound.

REFERENCES

1 G.R.A. Hunt, J. Chem. Educ., 53 (1976) 53.
2 R.J. Angelici, Synthesis and Technique in Inorganic Chemistry, W.B. Saunders, Philadelphia, 1968, p. 31.
3 R.B. King, Organometallic Syntheses, Vol. 1, Academic Press, New York, 1965, p. 114.