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Advanced Physical Chemistry

" Thermodynamic and Kinetic Study of Thermal Decomposition of Ferrocene "

By Doctoral Student

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Background

Ferrocene is a sandwich complex. It was first discovered in the early 1950's . In an attempt to synthesize fulvalene, Kealy and Pauson reacted dicyclopentadienyl magnesium bromide (CpMgBr) with anhydrous iron (III) chloride. Sublimation of the resulting mixture yielded orange crystals with a formula of $\text{C}_{10}\text{H}_{10}\text{Fe}$. Because of its unusual stability and special characteristics , the new iron compound attracted much attention . After many attempts to explain its structure , Wilkinson and Fischer separately proposed a sandwich structure in which the iron metal bonded to all of the five carbon atoms of each of the Cp rings. Soon the proposed structure was confirmed by the X-ray diffraction studies. Ferrocene name was given to the new iron compound due to ferrocene possessing aromatic properties similar to those of benzene.

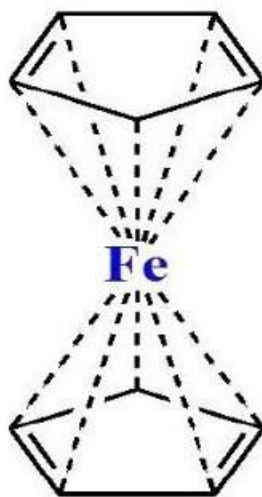
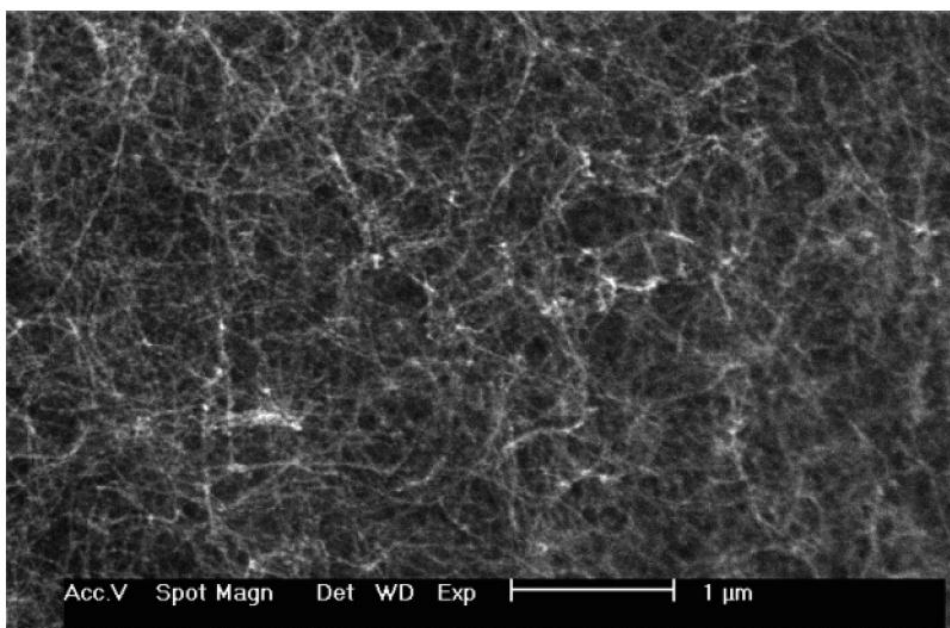


Figure (1) : Ferrocene structure

Introduction

Ferrocene has many interesting properties . In recent times, the organometallic compound ferrocene , $[(\text{C}_5\text{H}_5)_2\text{Fe}]$, has become an important precursor material for preparing iron oxide nanostructures through thermal decomposition, for example ferromagnetic micro/nanoparticles, iron oxide thin films, and single-walled / ferromagnetic-filled carbon nanotube as in the figure below:



Figure(2): SEM micrograph showing the morphology of as-grown SWCNT at 900 °C and 1 bar

Among all of the other applications of ferrocene decomposition, single-walled / ferromagnetic-filled carbon nanotube has attracted the most attention . The unique electrical and mechanical properties of these sp^2 – hybridized molecular nano-structure make them one of the most promising building blocks for Nano scale science and technology. This method has utilized ferrocene as the sole source for both catalytic Fe particles and carbon feedstock. The feasible control on the reaction parameters renders this technique a stable and reproducible route of synthesis of bulk-scale SWCNTs with defined diameter distribution . As no external carbon sources are required , it is possible to synthesize SWCNTs in a continuous manner at temperatures as low as 650 C. A further advantage is that ferrocene is not toxic.

In this essay, we are going to discuss the thermal decomposition of ferrocene, thermodynamically and kinetically in the presence of guest molecules of various kinds leading to iron oxides and the investigation of the correlation among the thermal decomposition reaction kinetics, morphology / physical characteristics of the reaction products, and the nature of the guest molecules.

There are two basic approaches to determine the reaction kinetic parameters or kinetic triplets (activation energy , frequency factor or rate of reaction, and most probable reaction mechanism function $g(\alpha)$ related to thermal decomposition using thermogravimetry (TG) data – (a) mechanistic and (b) nonmechanistic . At the

beginning , the present TG data analysis have been utilized the well-known classic equations of Freeman-Carroll, Kissinger , and Lozano et al. to estimate kinetic parameters related to the thermal decomposition of ferrocene. In addition, Arrhenius equation has been used to identify the most probable reaction mechanism function. Besides the Kissinger method, all other methods require single-heating rate-based TG data. Most importantly, the basic assumption for these methods is that the activation energy of decomposition reaction is unique and it does not depend on the extent of thermal decomposition at any instant of time. But as per the recommendation of the kinetics committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC), the multiple temperature program methods should be used to evaluate the reaction kinetic parameters reliably . Accordingly, two multiheating rate methods, called isoconversional methods, namely, improved iterative method and model-free method , are also employed to analyze the present TG data. The modern kinetics investigation procedure using multiheating rates is used to find out the most probable reaction mechanism function as well . In this article , the thermal decomposition study of ferrocene have been reported by thermogravimetry. In addition, an estimation of the reaction kinetic parameters have been studied based on the mathematical analysis of thermogravimetric profiles of ferrocene and, on the other hand, variation of activation energy values (estimated by various methods) was discussed with the extent of thermal decomposition to reveal the applicability of the methods based on single-heating rate over the ICTAC recommendation for single-step solid state thermal reactions.

The thermodynamic Parameters, from the theory of the activated complex (transition state) of Eyring , the following general equation may be written:

$$A = \frac{e\chi k_B T_p}{h \exp(\Delta S^*/R)},$$

The change of the entropy ΔS^* may be calculated according to the following formula:

$$\Delta S^* = R \ln \left(\frac{Ah}{e\chi k_B T_p} \right).$$

Since

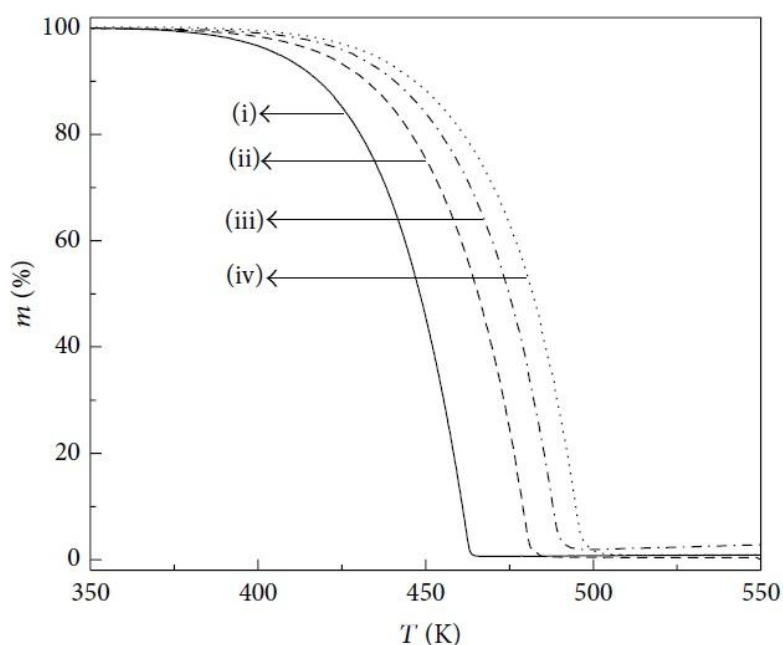
$$\Delta H = E^* - RT_p,$$

the changes of the enthalpy ΔH^* and Gibbs free energy ΔG^* for the activated complex formation from the precursor can be calculated using the well-known thermodynamical equation:

$$\Delta G^* = \Delta H^* - T_p \Delta S^*.$$

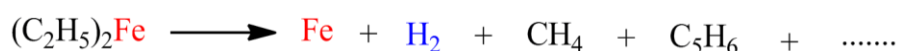
The calculations of reaction kinetic parameters, using the above-stated equations, were based on a program compiled in MATLAB.

Ferrocene (C_5H_5)₂Fe has a “sandwich structure” of two parallel cyclopentadienyl rings with an iron in the center between these rings. It is solid at room temperature and thermally decomposes at 448 K and its boiling point is 522K. Figure 3 shows the TG profiles of ferrocene obtained under four different heating rates (5, 10, 15, and 20 Kmin⁻¹). Each TG profile confirms a one-step decomposition process for this material and represents the relationship of the residual mass with temperature during thermal decomposition. However, this decomposition takes place in temperature ranges 349–465K, 345–485K, 356–498K, and 385–511K for 5, 10, 15, and 20Kmin⁻¹ heating rates, respectively, and the thermal reaction becomes maximum at ~448K in all cases of heating rates and is completed with almost ~100% mass loss beyond ~510K. Melting point of ferrocene is 448K.



Figure(3): Thermogravimetric profiles of ferrocene obtained under different heating rates : (i) 5 K min⁻¹, (ii) 10 K min⁻¹, (iii) 15 K min⁻¹, and (iv) 20 K min⁻¹

In the temperature range from ~870K to ~1420 K ferrocene further decomposes. According to Leonhardt et al. , at temperatures above ~770K, gaseous ferrocene decomposes spontaneously to form metallic iron according to the following reaction:



This means that in this temperature range solid or liquid like Fe particles and different kinds of hydrocarbons may exist in the reaction medium. Thus, the presently observed thermal decomposition indicates that the sublimation of ferrocene which takes place during solid state reaction and no further conversion to liquid or solid Fe has been observed as no increase in mass has been recorded in the TG profile.

At this point it has to be noted that TG deals with a very small amount of sample mass. At higher temperatures when the further conversion of sublimated ferrocene to liquid or solid Fe takes place, it is quite unlikely to be detected by the TG considering the converted sample mass as well as the presently used sample cell geometry.

Utilizing the TG data of the thermal decomposition of ferrocene, the activation energy values for the single-step reaction process were calculated from the slope of (i) the $\ln W$ versus $1/T$ plot using (1) and of (ii) the $\ln (\beta/T^2P)$ versus $-1/T$ plot using (2) and are shown in Table 1.

$\alpha^{\#}$	Activation energy, $E/\text{kJ}\cdot\text{mole}^{-1}$							Frequency factor A/min^{-1}			
	(1)	(2)	(3)	(4)	(7)	(8)	(13)	$\beta = 5/\text{K min}^{-1}$	$\beta = 10/\text{K min}^{-1}$	$\beta = 15/\text{K min}^{-1}$	$\beta = 20/\text{K min}^{-1}$
0.1					68.01	68.01	68.02	2.3×10^4	2.29×10^4	2.41×10^4	2.33×10^4
0.2					67.66	67.66	67.68	8.11×10^4	8.09×10^4	8.54×10^4	8.25×10^4
0.3					66.34	66.34	66.36	1.24×10^5	1.25×10^5	1.33×10^5	1.28×10^5
0.4					66.42	66.42	66.44	2.22×10^5	2.24×10^5	2.37×10^5	2.28×10^5
0.5	64.18	88.6	77.6	87.7	66.42	66.42	66.44	3.43×10^5	3.45×10^5	3.66×10^5	3.51×10^5
0.6					67.21	67.21	67.23	6.06×10^5	6.04×10^5	6.39×10^5	6.16×10^5
0.7					67.40	67.40	67.40	8.55×10^5	8.51×10^5	9.00×10^5	8.69×10^5
0.8					69.41	69.41	69.42	1.92×10^6	1.88×10^6	1.97×10^6	1.93×10^6
0.9					68.34	68.34	68.35	1.80×10^6	1.77×10^6	1.87×10^6	1.81×10^6

[#] α : extent of conversion.

Note: $A = 1.87 \times 10^5$ from (1) and 1.05×10^8 from (4).

Table (1): Values of the activation energy (E) estimated following different equations and the frequency factor (A) for different heating rates (β) for thermal decomposition of ferrocene.

Again the kinetic parameters for the decomposition of ferrocene were estimated and are presented in Table 1. It is noted that the rate of reaction for the decomposition of ferrocene varies in the range of $10^4 \sim 10^6 \text{ min}^{-1}$. Interestingly, the observed dependence of A value with α indicates that the reaction rate cannot be assumed as a constant for the nonisothermal decomposition process of ferrocene. From Table 1 one can also note that

the A value determined by using (1) is $\sim 10^5 \text{ min}^{-1}$, while that from (4) is $\sim 10^8 \text{ min}^{-1}$ where the former lies well within the range determined. The low A values often indicate a surface reaction. If the thermal reactions are not dependent on surface area, the low A value indicates a “tight” complex, while the higher A value indicates a “loose” complex. Therefore, in the present case the thermal decomposition reaction of ferrocene deals with a “loose” complex. The observed T_p values correspond to $\alpha = \sim 0.9$ in the α versus T plots. Based on the estimated values of the activation energy E^* and frequency factor A for $\alpha = 0.9$ for thermal decomposition of ferrocene under different heating rates (see Table 1), the thermodynamic parameters ΔS^* , ΔH^* and ΔG^* for the formation of an activated complex from the precursor were calculated according to thermodynamic equations and are presented in Table 2. These values are calculated at the peak temperature T_p in the differential thermogravimetry curve for the corresponding heating rates, since this temperature characterizes the highest rate of the reaction during the single-step thermal decomposition.

$\beta/\text{K}\cdot\text{min}^{-1}$	T_p/K	$\Delta S/\text{J}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$	Average value of $\Delta S/\text{J}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$	$\Delta H/\text{kJ}\cdot\text{mole}^{-1}$	Average value of $\Delta H/\text{kJ}\cdot\text{mole}^{-1}$	$\Delta G/\text{kJ}\cdot\text{mole}^{-1}$	Average value of $\Delta G/\text{kJ}\cdot\text{mole}^{-1}$
5	462	-171.12		64.49		143.56	
10	479	-171.42	-171.45	64.36	64.34	146.47	146.81
15	488	-171.57		64.28		148.01	
20	495	-171.69		64.22		149.01	

Table(2): Values of the thermodynamic parameter for thermal decomposition of ferrocene for different rates.

As can be seen from Table 2, the values of ΔS , ΔH , and ΔG obtained under different heating rates are independent of heating rates, and thus we discuss the average values of these parameters only. The value of ΔS for ferrocene is negative. It means that the corresponding activated complex had lower entropy or a higher degree of ordering than the precursor state. Thus, if we denote the entropy of the precursor and the activated complex as S_0 and S_I , respectively, then $S_0 > S_I$ for thermal decomposition of ferrocene. In the terms of the theory of an activated complex [27–30], the thermal decomposition of ferrocene may be further classified into “slow” stage with negative entropy change.

In summary, Ferrocene undergoes 100% thermal decomposition. A comparison of the kinetic parameters for the single-step thermal decomposition reaction of ferrocene estimated here by different methods has been made. The activation energy values

determined are in conformity with previously reported values. The activation energy values are found to be independent of the extent of conversion, whereas the reaction rate strongly depends on the same. From the present analysis, it has to be noted that the activation energy and the frequency factor values determined by Freeman-Carroll equation are quite similar to that obtained by multiheating rate-dependent isoconversional methods as recommended by ICTAC. On the other hand, the reaction mechanism-three-dimensional diffusion reaction for the thermal decomposition of ferrocene predicted by Lozano et al.'s method is basically similar to that obtained by using isoconversional methods following ICTAC recommendation. Thus, it seems that for single-step thermal decomposition reactions like the present one, the methods based on single-heating rate program may provide reliable kinetic parameters as obtained by multiple-heating rate programs, and thus single-heating rate-based methods could be applicable for such single-step thermal decomposition reactions. However, this is an open question which needs to be verified for good number of such thermal decomposition reactions. It is our conjecture that the activation energy of solid state reaction in such a case is either unique or nearly independent of the extent of thermal decomposition. Ferrocene when heated alone above $\sim 770\text{K}$ does not produce any traceable solid material detectable in the TG profile, but when it is heated together with oxalic acid the solid hematite product is formed at $\sim 450\text{K}$. This may imply that oxalic acid catalyzes the thermal decomposition of ferrocene.

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