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THE THERMAL DECOMPOSITION OF POLY-4,4'-OXYDIPHENYLENE PYROMELLITIMIDE

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ABSTRACT

The thermal decomposition of Vespel SP-1 (poly-4,4'-oxydiphenylene pyromellitimide) has been investigated using thermogravimetry. Weight versus temperature curves in dry air, in dry argon and under vacuum are reported. Vespel SP-1 undergoes a partial decomposition (carbonization) above 470°C in argon and under vacuum resulting in a weight loss of approximately 35%. In air a second decomposition step (oxidation) is observed which results in a weight loss of nearly 100%. Samples were decomposed isothermally in argon to investigate the carbonization step and these partially decomposed samples were then heated isothermally in air to study the oxidation process. Activation energies determined are 76.5 ±1.3 kcal/mole for the first step in argon and 24.5 ±0.7 kcal/mole for the final decomposition in air.

INTRODUCTION

DuPont's Vespel SP-1 (poly-4,4'-oxydiphenylene pyromellitimide) has been used as an insulating material in molten salt electrochemical power sources which operate at internal temperatures in excess of 400°C. To further determine Vespel's utility in such applications, its thermal stability has been studied in air, in argon and under vacuum. A number of investigators have studied poly-4,4'-oxydiphenylene pyromellitimide in recent years. Thermograms have been obtained at constant heating rates in air[1–3], in helium[1,4] and in a vacuum[2,3]. Isothermal decomposition has also been investigated in air[1,4–6], in helium[1,4] and in a vacuum[5]. Bruck[7] reports activation energies of decomposition in air and under a vacuum, based on weight loss data. Dine-Hart and Wright[6] also determined activation energies in air based on weight loss rates. Heacock and Berr[1] measured activation energies on the basis of changes in physical properties. Activation energies obtained from rates of CO and CO_2 production are reported by Gay and Berr[8].

The products of the decomposition have been identified by several investigators[2,3,7–9] and reaction mechanisms have been postulated. Other related papers concerning the thermal decomposition of poly-4,4'-oxydiphenylene pyromellitimide have been published by Nishizaki and Fukami[10], Bruck[11,12] and Gordon[13]. The results of this study add significant new data to that reported in the literature.

EXPERIMENTAL

Poly-4,4′-oxydiphenylene pyromellitimide was obtained from E. I. duPont under the trade name Vespel SP-1. This type of Vespel contains no additives and was used as received except that absorbed moisture was removed by heating at 250°C.

Thermograms were obtained using a Cahn Vacuum Electrobalance System which included a Model RG electrobalance and a Model 3430 furnace. A Cahn Time Derivative Computer was used to measure rate of weight change. Temperature was controlled using a Research, Inc. Model 5500/624A Programmer/Controller and measured with a Chromel–Alumel thermocouple suspended inside the hangdown tube.

Weight versus temperature curves were obtained for samples in dynamic dry air, in dynamic dry argon, and under vacuum using a heating rate of 2.15°C/min. Weight and rate of weight change versus time curves under isothermal conditions were obtained only in air and argon. Flow rates of 90 ml/min were used with both argon and air atmospheres, while the vacuum employed was of the order of 10^{-3} mm Hg. The method used for the isothermal investigations was to heat a sample in an argon atmosphere until the rate of weight loss decreased by two orders of magnitude. This partially decomposed sample was then cooled to room temperature, the atmosphere was changed from argon to air, and the sample was again heated at constant temperature until the rate of weight loss passed through its maximum value. All samples weighed approximately 15 mg.

RESULTS AND DISCUSSION

Weight versus temperature curves for Vespel SP-1 are shown in Fig. 1. The curves in argon and under vacuum are identical and represent primarily carboni-

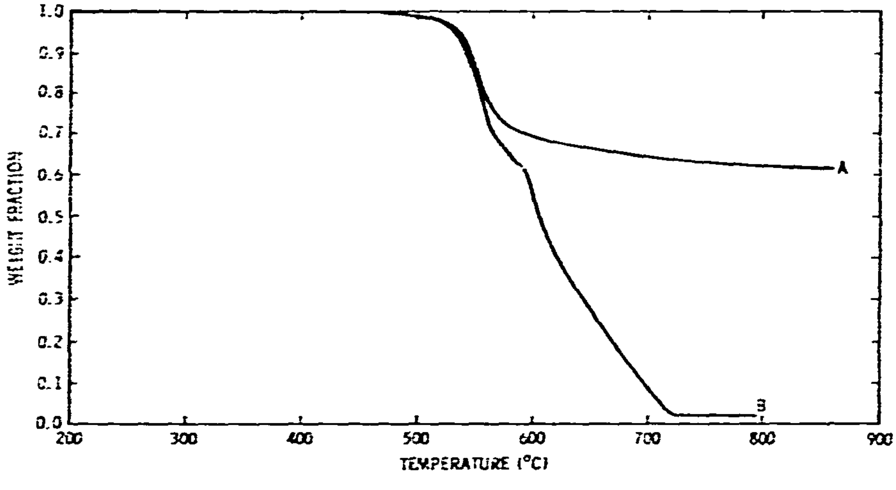

Fig. 1. Thermogravimetric curves for Vespel SP-1. (A) 90 ml/min dry argon and 10^{-3} mm Hg vacuum; (B) 90 ml/min dry air. Heating rate, 2.15°C/min.

zation of the sample. These results are virtually the same as those reported by other workers in He[1,4] and in vacuo[2,3]. The sample begins to lose weight at about 470°C, and a plateau is reached in the vicinity of 800°C at approximately 60–65% of the original sample weight.

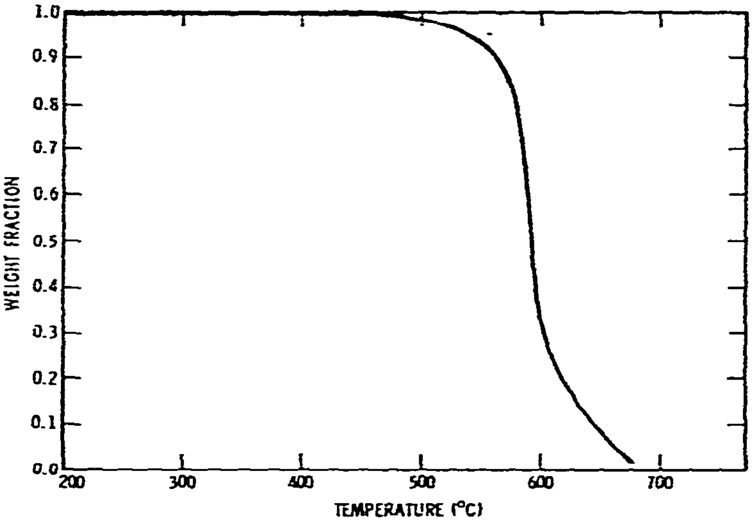

Fig. 2. Thermogravimetric curve for H-film in dry air (Heacock and Berr[1]).

In air, however, our results differ from those previously reported[1–3] in that the break observed after a 35–40% weight loss in the present investigation was not reported by previous workers. A thermogram obtained by Heacock and Berr[1] for poly-4,4'-oxydiphenylene pyromellitimide is shown in Fig. 2 for comparison. This difference cannot be explained on the basis of heating rates since Jewell[3] used a rate of 1°C/min, Ehlers *et al.*[2] 2.5°C/min and Heacock and Berr[1] 3°C/min. The value of 2.15°C/min used in the present investigation falls within the range of rates previously used. The difference may result from the method of sample preparation or from the particular physical form of poly-4,4'-oxydiphenylene pyromellitimide used. Ehlers *et al.*[2] and Jewell[3] used materials which they prepared in their laboratories and Heacock and Berr[1] worked with H-film. The break observed in this investigation is caused by the occurrence of two different successive decomposition processes. The first step is the carbonization of the sample which occurs in air, in argon or under vacuum. In the presence of oxygen this is followed by the oxidation of carbon to form carbon monoxide and carbon dioxide[2,3,7–9].

Both of these decomposition processes were investigated isothermally to determine reaction rates and activation energies. The initial carbonization reaction was studied in dry argon; samples which had undergone the carbonization step were then used to investigate the final oxidative decomposition in dry air. Representative weight versus time curves are shown in Fig. 3 for the first decomposition in argon and in Fig. 4 for the final decomposition in air. The experimentally determined weight loss

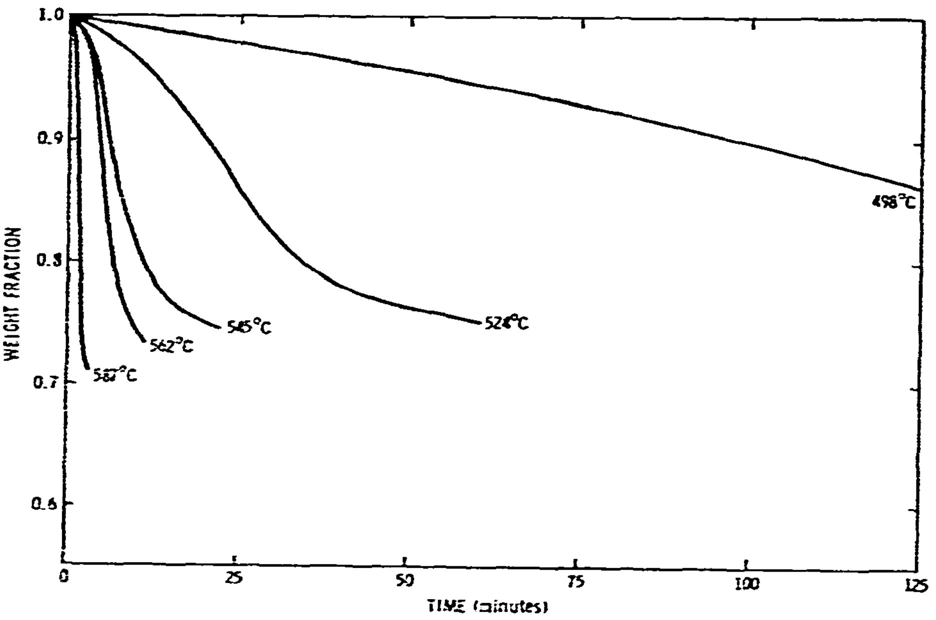

Fig. 3. Isothermal weight loss of Vespel SP-1 in dry argon.

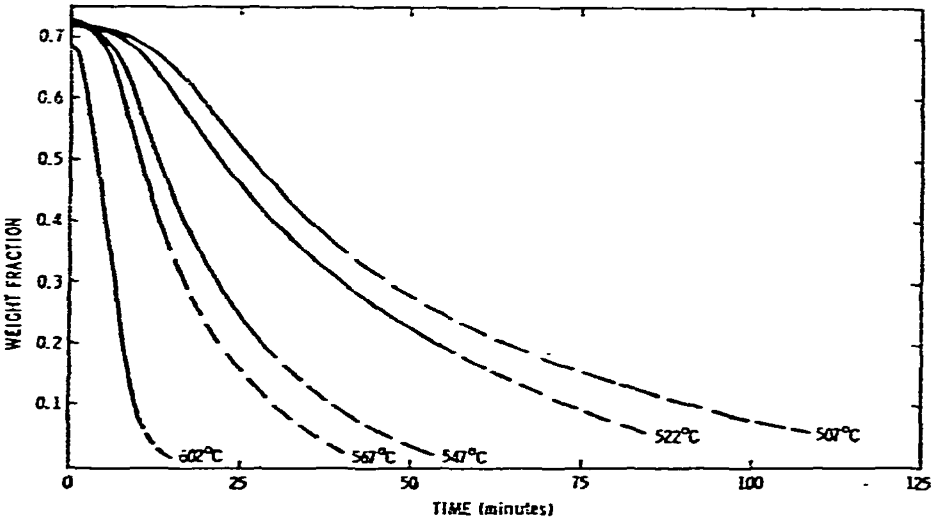

Fig. 4. Isothermal weight loss of partially decomposed Vespel SP-1 in dry air.

in air is shown by the solid lines in Fig. 4. The broken lines represent the expected completion of the decomposition based on previously obtained data.

The differences observed in the initial stages of the decomposition in air (Fig. 4) are dependent upon the extent of prior decomposition which had occurred in the argon atmosphere. These differences do not affect the determination of reaction rates and the resulting calculation of activation energies.

Maximum rates of weight loss in air and argon were determined from the curves represented in Figs. 3 and 4 for each temperature using the Cahn Derivative Computer. These values are shown in Table 1 for argon and in Table 2 for air.

TABLE 1

MAXIMUM DECOMPOSITION RATE FOR VESPEL SP-1 IN ARGON AT VARIOUS TEMPERATURES

Temperature (°C)	*Maximum decomposition rate (Weight fraction/min)*
498	0.00120
517	0.00454
524	0.00735
541	0.0190
545	0.0230
562	0.0526
576	0.132
587	0.233

TABLE 2

MAXIMUM RATE OF OXIDATIVE DECOMPOSITION FOR VESPEL SP-1[a] IN AIR AT VARIOUS TEMPERATURES

Temperature (°C)	*Maximum decomposition rate (Weight fraction/min)*
507	0.0123
522	0.0175
540	0.0228
547	0.0276
567	0.0357
588	0.0558
602	0.0712

[a] Sample subjected to prior partial decomposition in argon.

From these maximum decomposition rates activation energies were computed by least squares analysis using the Arrhenius equation, $k = Ae^{-E_a/RT}$ where k is the rate constant (in this case the maximum rate), A is a frequency factor, E_a is the activation energy, R is the gas constant and T is temperature in degrees Kelvin. Arrhenius plots are shown in Figs. 5 and 6 for argon and air respectively.

The activation energy calculated for the carbonization process in argon is 76.5 ± 1.3 kcal/mole. This value is compared with literature values in Table 3 and agrees well with the value of 74 kcal/mole determined by Bruck[7] from weight loss data in a vacuum.

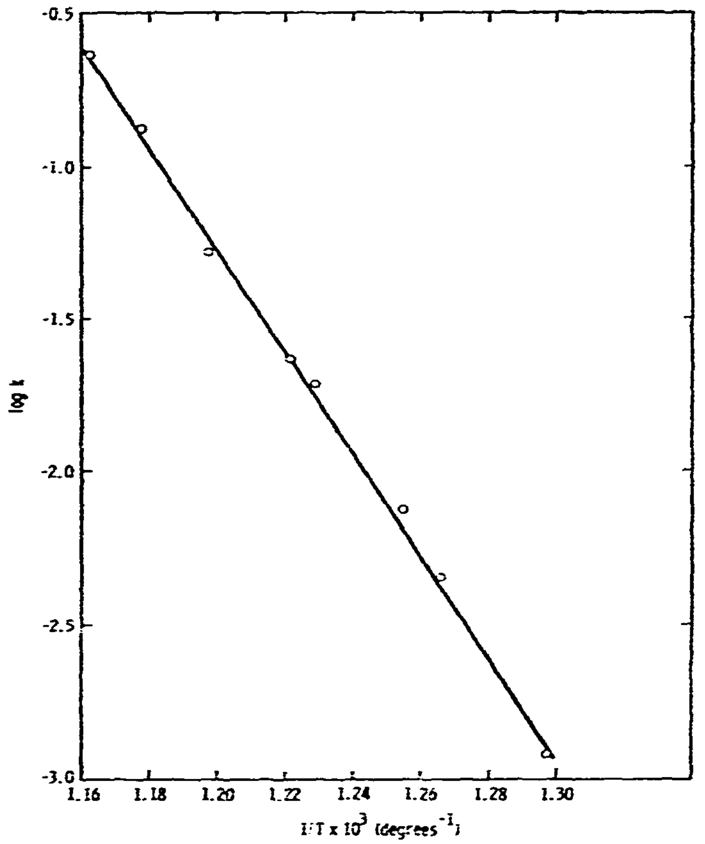

Fig. 5. Arrhenius plot for maximum decomposition rates of Vespel SP-1 in dry argon.

TABLE 3

COMPARISON OF ACTIVATION ENERGIES (E_a) REPORTED FOR THE THERMAL DECOMPOSITION OF POLY-4,4'-OXYDIPHENYLENE PYROMELLITIMIDE

Material	*Method*	*Atmosphere*	E_a *(kcal/mole)*	*Reference*
H-film	weight loss	air	33	7
Lab. prepared	weight loss	air (60–70% R.H.)	33.0	6
H-film	loss of physical properties	air (dry)	39.9	1
Lab. prepared	weight loss	air (dry)	45.1	6
H-film	loss of physical properties	helium (dry)	54.0	1
H-film	weight loss	vacuum	74	7
Vespel SP-1	weight loss	argon (dry)	76.5 ± 1.3	this work

The activation energy for the oxidative decomposition in air was calculated as 24.5 ± 0.7 kcal/mole. Comparison with literature values is not possible because this is

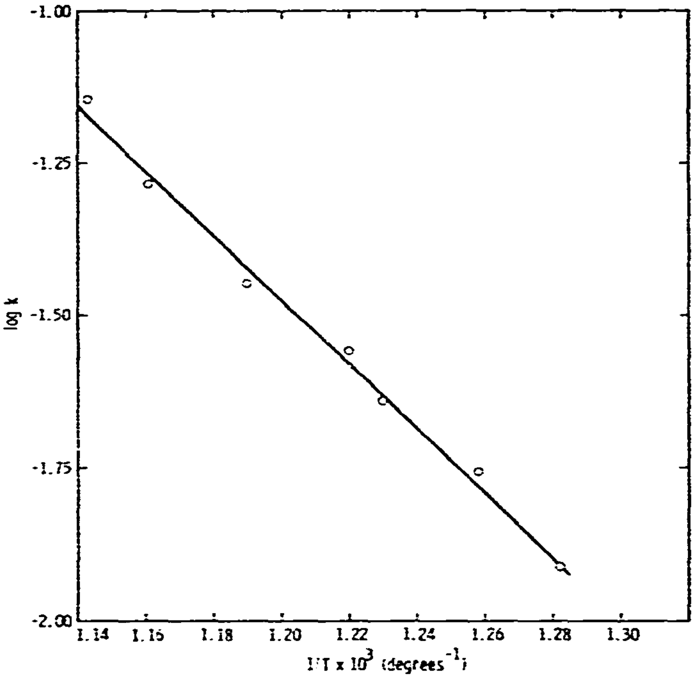

Fig. 6. Arrhenius plot for maximum oxidative decomposition rates of partially decomposed Vespel SP-1 in dry air.

the first time that the second (oxidative) step in the decomposition has been studied by itself. Previous investigations in air were concerned with the overall thermal decomposition which involved both the carbonization and the oxidation processes. However, it will be noted that the activation energies reported by previous workers for the overall decomposition in air are between the values reported in this investigation for the two individual processes. This is as expected since the overall process is a combination of the two.

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