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KINETICS OF INTERCALATE DESORPTION FROM CARBON FIBERS INTERCALATED WITH BROMINE

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Abstract—This paper reports the kinetics of intercalate desorption from pitch-based carbon fibers intercalated by exposure to Br_2. The kinetics was studied by thermogravimetric analysis of brominated Thornel P-100 and P-X-7 carbon fibers of Amoco Corp., as P-X-7 was more graphitic than P-100. Comparison was made with previous kinetic data on highly oriented pyrolytic graphitic (HOPG) intercalated with bromine. The activation energies of desorption below 100°C were 9, 12, and 17 kcal/mol Br_2, respectively, for P-100, P-X-7, and HOPG. The values above 100°C were 8, 5, and 4 kcal/mol Br_2, respectively, for P-100, P-X-7, and HOPG. A high degree of order of the intercalate increases the activation energy below 100°C, whereas a high degree of graphitization decreases the activation energy above 100°C. Brominated P-100 retained a stable bromine concentration of 17.5 wt.% up to at least 200°C. This thermal stability is attributed to the relatively high activation energy of desorption of brominated P-100 above 100°C.

Key Words—Carbon fibers, intercalation, bromine, desorption, kinetics.

1. INTRODUCTION

Pitch-based carbon fibers (Thornel P-100 of Amoco) brominated by exposure to Br_2 have recently received much attention because the bromination decreased the electrical resistivity from 250 to 52 $\mu\Omega$.cm and because this low resistivity was not changed over a period exceeding three years of exposure to the atmosphere[1]. Furthermore, the brominated P-100 fibers were stable in resistivity up to 200°C[2]. Bromine stood out as the intercalate that gave the best stability, compared to other intercalates such as ICl, $CuCl_2$ and $NiCl_2$[1]. The low electrical resistivity is attractive for electromagnetic interference shielding and for lightning protection of aircrafts.

Previous stability studies on brominated Thornel P-100 carbon fibers were made by monitoring the electrical resistivity[1,2]. This paper provides a complementary study by monitoring the bromine content, which is directly related to the chemical or environmental stability. Furthermore, this study provides information on the kinetics of bromine desorption from the fibers. From this information, we provide an explanation for the exceptional stability of brominated P-100 fibers.

Thornel P-100 carbon fibers brominated by exposure to Br_2 are intercalated, but the intercalate layers do not exhibit in-plane order at room temperature[3]. In contrast, highly oriented pyrolytic graphite (HOPG) and highly graphitic carbon fibers (e.g., Amoco's P-X-7 and du Pont's E-130) that have been brominated by exposure to Br_2 exhibit in-plane superlattice order at room temperature and up to 100°C, at which temperature in-plane melting occurs[4,5]. As the melting at 100°C is known to affect the kinetics of bromine desorption from HOPG[6], it is interesting to investigate its effect in the case of carbon fibers.

The thermal stability of the resistivity increased with decreasing degree of graphitization, as shown by comparing the behavior of Amoco P-75, P-100, and P-120 carbon fibers (listed in order of increasing degree of graphitization)[2]. Therefore, this paper also investigates how the structural difference between P-100 and more highly graphitic fibers affects the desorption kinetics.

2. EXPERIMENTAL

2.1 *Sample preparation*

Two types of pitch-based carbon fibers were used. They were Thornel P-100 and P-X-7, both kindly provided by Amoco Corp. Although both are among the most graphitic types of carbon fibers, P-X-7 is even more graphitic than P-100. The P-100 fibers are commercially available, but the P-X-7 fibers are experimentally available.

Bromination of either type of fibers was carried out by exposure of the fibers (without resin sizing) to bromine vapor in air at room temperature for at least six days.

2.2 *Experimental method*

The bromine content in the fibers was obtained by measuring the weight of the fibers before and after bromination. In order to study the bromine desorption kinetics after bromination, the weight of the fibers was measured in air as a function of time and temperature up to 200°C. Such temperatures are too low for weight loss due to oxidation of carbon fibers, as independently shown by mass spectrometric observation of the evolved CO_2 as a function of temperature[7].

The thermogravimetric measurement was performed by using a Perkin-Elmer electronic microbalance (Autobalance Model AD-2Z), which has a maximum sensitivity of 0.1 μg. The sample was placed on a platinum pan suspended by a platinum hangwire. A quartz tubing (25.4 mm inside diameter) enclosed the hangwire and the sample pan. During measurement the tube was slowly purged with nitrogen at a rate of approximately 15 cm^3/min. A low mass furnace surrounded the sample pan and was controlled by a Theall Engineering Model TP-2000 temperature programmer capable of either isothermal or scanning temperature control. The sample temperature was measured by placing a chromel-alumel thermocouple immediately below (within 2 mm of) the sample pan.

2.3 *Experimental results*

2.3.1 *Scanning thermogravimetric analysis* (*TGA*). Figures 1 and 2 show the thermogravimetric data of brominated P-100 and brominated P-X-7, respectively. The data for brominated P-100 were obtained after five days of room temperature desorption; the data for brominated P-X-7 were obtained after three days of room temperature desorption. The samples were heated at a rate of 10°C/min and the weight of each sample was about 20 mg. Both sets of data show an onset of significant bromine desorption at 100°C, the temperature for in-plane melting of graphite intercalated with bromine[8]. However, a clearer onset was observed for brominated P-X-7 than brominated P-100.

2.3.2 *Isothermal desorption.* Isothermal desorption was studied on brominated P-100 and brominated P-X-7. The weight of each sample was about 20 mg.

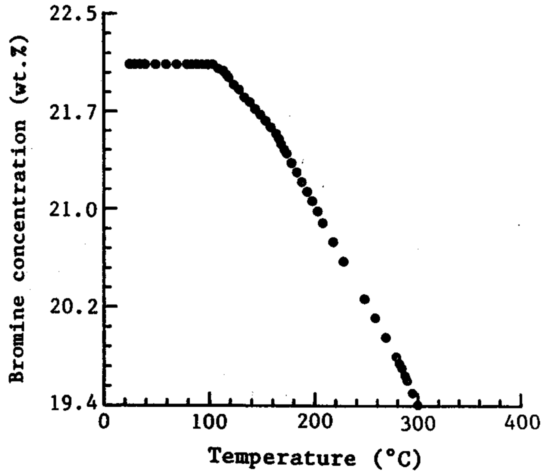


Fig. 2. Bromine concentration (% by weight of parent fibers) versus temperature during heating for brominated P-X-7 fibers.

2.3.2.1 *Brominated P-100.* Figure 3 shows the bromine concentration as a function of time for brominated P-100 desorbed at 60, 70, 80, and 90°C. During the early part of the desorption process, the desorption rate increased as the temperature increased. Complete desorption did not occur because a significant portion of the original bromine (equivalent to 20 wt.% of the parent fibers) was retained by the fibers even after a long desorption time. This stable bromine concentration of 20 wt.% was attained at all temperatures below 100°C (i.e., 60, 70, 80, and 90°C), although the time needed to attain stability increased with decreasing temperature.

In analyzing the data, the stable bromine concentration was subtracted from the total bromine concentration to yield the "desorbable" bromine con-

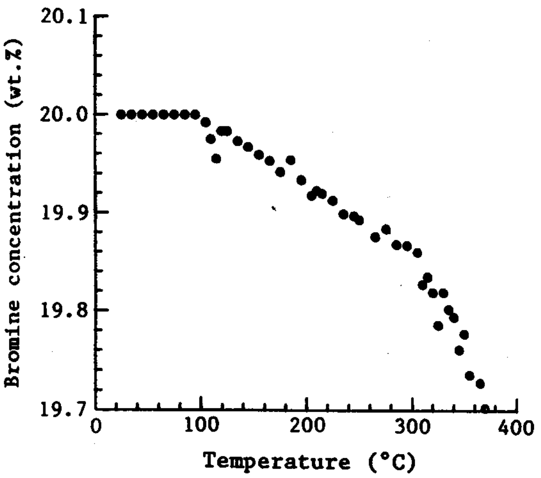


Fig. 1. Bromine concentration (% by weight of parent fibers) versus temperature during heating for brominated P-100 fibers.

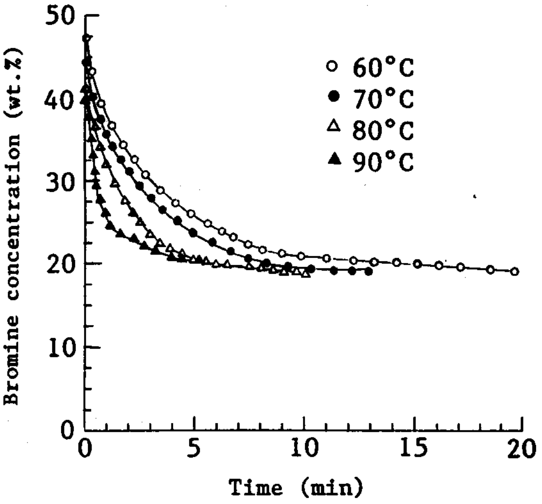


Fig. 3. Bromine concentration (% by weight of parent fibers) versus time at different constant temperatures below 100°C for brominated P-100 fibers.

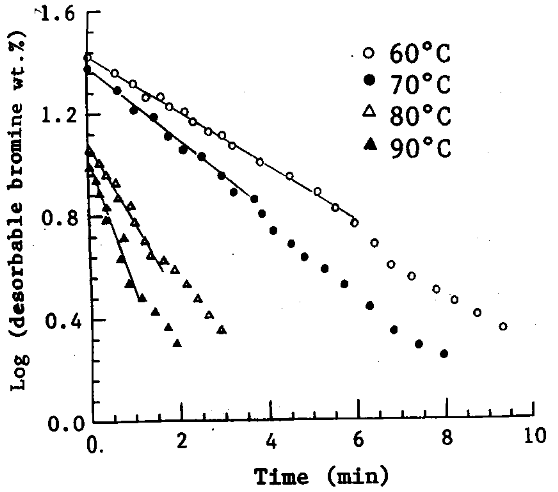


Fig. 4. Logarithm of the desorbable bromine concentration versus time at different constant temperatures below 100°C for brominated P-100 fibers.

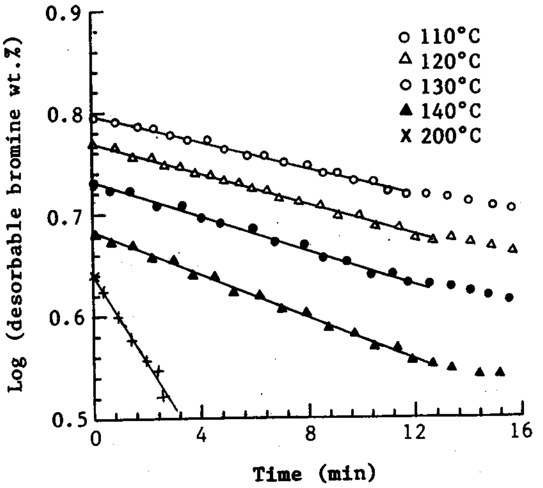


Fig. 6. Logarithm of the desorbable bromine concentration versus time at different constant temperatures above 100°C for brominated P-100 fibers.

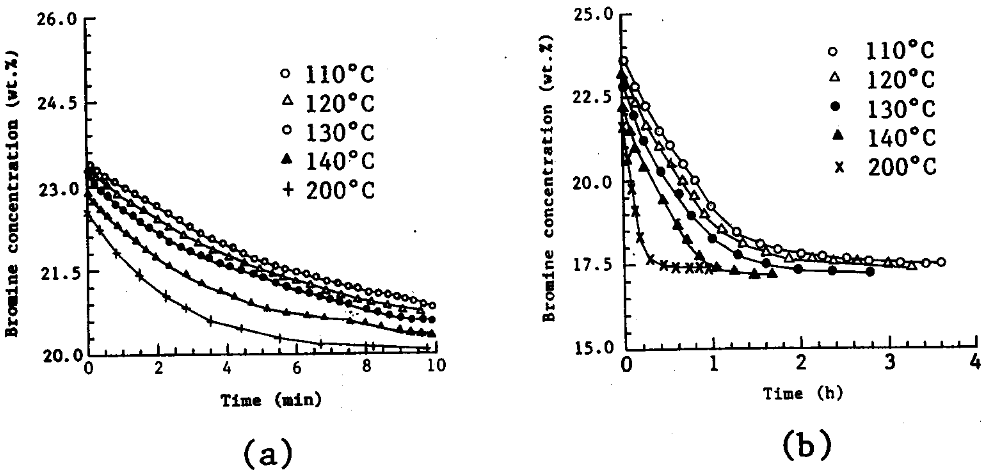
centration C^*. In other words,

$$C^* = \frac{M_{Br} - M_S}{M_C}, \quad (1)$$

where M_{Br} is the mass of bromine at a given time, M_S is the mass of bromine at the stable bromine concentration and M_C is the mass of the parent fibers. Figure 4 shows the logarithm of the desorbable bromine concentration, log (C^*), as a function of time.

Desorption curves for desorption at temperatures above 100°C are shown in Fig. 5(a) for times up to 10 min and in Fig. 5(b) for times up to 4 h. Because of the high desorption rate at 100°C (see section 2.3.1), it was impossible to maintain a high bromine concentration above 100°C. As a result, measurements above 100°C could only be performed on relatively dilute samples (less than 25 wt.% bromine). The temperatures chosen for isothermal measurements were 110, 120, 130, 140, and 200°C. The desorption rate increased as the temperature increased, as in the case of desorption below 100°C. As shown in Fig. 5(b), desorption at these temperatures led to a stable bromine concentration of 17.5 wt.%. The desorbable bromine concentration was obtained using eqn (1) with this value of the stable bromine concentration, and its logarithm was plotted against time, as shown in Fig. 6.

2.3.2.2 *Brominated P-X-7.* Figure 7 shows the bromine concentration as a function of time for brominated P-X-7 desorbed at 60, 70, 80, and 90°C. At these temperatures below 100°C, a bromine concentration of 22 wt.% remained in the fibers even



(a) (b)

Fig. 5. Bromine concentration (% by weight of parent fibers) versus time at different constant temperatures above 100°C for brominated P-100 fibers. (a) up to 10 min; (b) up to 4 h.

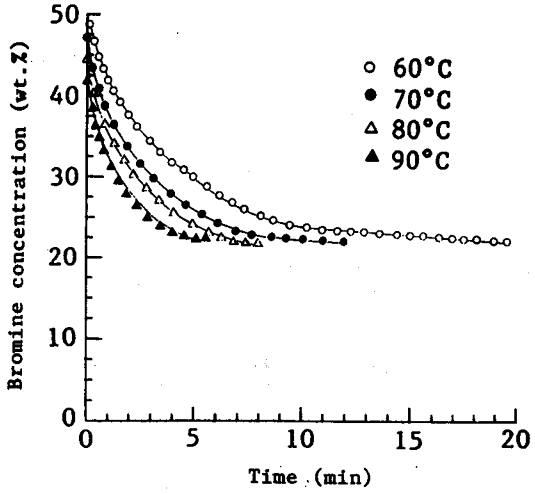


Fig. 7. Bromine concentration (% by weight of parent fibers) versus time at different constant temperatures below 100°C for brominated P-X-7 fibers.

after very long desorption times. This amount was thus subtracted from the total amount of bromine to yield the "desorbable" portion of the bromine, as shown in Fig. 8. Comparison of brominated P-X-7 (Figs. 7 and 8) with brominated P-100 (Figs. 3 and 4) shows that the desorption rate of brominated P-100 at temperatures below 100°C was faster than that of brominated P-X-7.

Figure 9 shows the bromine concentration as a function of time for brominated P-X-7 desorbed at 110, 130, and 140°C. After long times of desorption, the fibers became stable at 17.5 wt.% bromine, as shown in Fig. 9(b). The desorbable bromine concentration is shown versus time in Fig. 10. Comparison of Figs. 9 and 5 shows that the desorption rate of brominated P-X-7 at temperatures above 100°C was faster than that of brominated P-100.

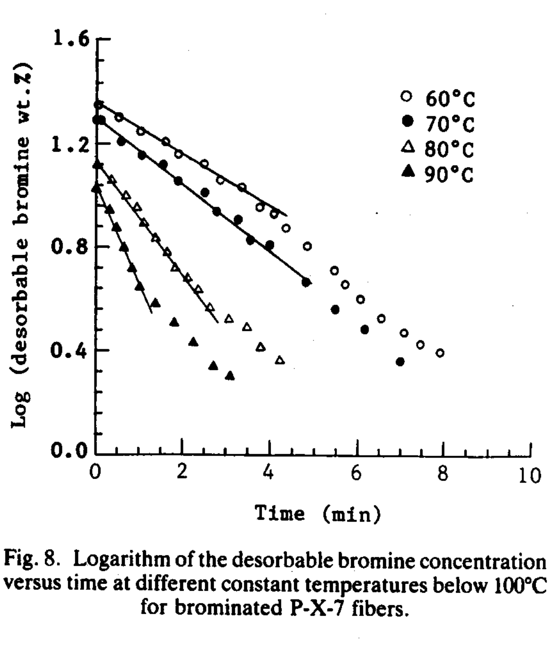


Fig. 8. Logarithm of the desorbable bromine concentration versus time at different constant temperatures below 100°C for brominated P-X-7 fibers.

2.3.3 *Analysis.* The desorption process is probably diffusion controlled, as suggested by the kinetics of desorption from brominated HOPG[6] and the kinetics of bromination of HOPG[9]. The desorbable bromine concentration remaining in the fibers at time t is then approximately proportional to $\exp(-kt)$, where k is the rate constant for the desorption process[10]. Hence, the rate constant k can be determined from the initial slope of the plot of the logarithm of the desorbable bromine concentration versus time. That is,

$$-k = \frac{d(\ell n C^*)}{dt}, \tag{2}$$

For a diffusion process, the rate constant k increases with temperature in the form

$$k = k_o \exp\left(-\frac{E_D}{k_B T}\right), \tag{3}$$

where k_o is a constant of proportionality, E_D is the activation energy of desorption, and k_B is the Boltzmann's constant and T is the temperature in K. A plot of log k verus $1/T$ yields a straight line, the slope of which is $-0.434\ E_D/k_B$.

The desorption process at high bromine concentrations (above 26 wt.%) could be studied only at temperatures below 100°C, because of the more severe desorption above 100°C.

Arrhenius plots that give the activation energy E_D are shown in Fig. 11 for temperatures below 100°C and in Fig. 12 for temperatures above 100°C. Table 1 lists the values of E_D obtained.

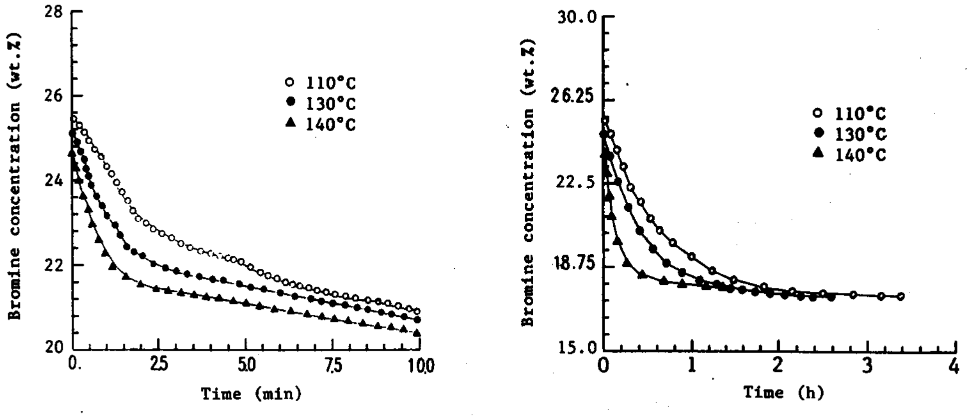
3. CONCLUSION AND DISCUSSION

The stable bromine concentration is a technologically important quantity because practical use of brominated fibers involves the stable form of the fibers. Table 2 lists the stable bromine concentrations for P-100 and P-X-7 fibers. The stable bromine concentration below 100°C is higher for P-X-7 than P-100, but is the same for the two types of fibers above 100°C.

The desorption rate of brominated P-100 is faster than that of brominated P-X-7 at temperatures below 100°C, but is slower than that of brominated P-X-7 at temperatures above 100°C.

The activation energy of desorption from brominated P-100 is lower than that of brominated P-X-7 at temperatures below 100°C, but is higher than that of brominated P-X-7 above 100°C.

The values of the activation energy of desorption are similar for brominated P-100 below 100°C and above 100°C, whereas the values are quite different



(a) (b)

Fig. 9. Bromine concentration (% by weight of parent fibers) versus time at different constant temperatures above 100°C for brominated P-X-7 fibers. (a) up to 10 min; (b) up to 4 h.

for brominated P-X-7 below 100°C and above 100°C. A substantial difference in the activation energy of desorption had been reported for brominated HOPG below 100°C and above 100°C[6], as shown in Table 1, which indicates that the activation energy of desorption increases with increasing degree of graphitization below 100°C, but decreases with increasing degree of graphitization above 100°C. The increase of the activation energy with increasing degree of graphitization below 100°C is due to the fact that the degree of intercalate order increases with increasing degree of graphitization. In this context, it should be noted that in-plane intercalate order is absent in brominated P-100 below 100°C, but is present in brominated P-X-7 and brominated HOPG below 100°C. It is further expected that staging is clearer in brominated HOPG than brominated P-X-7. Above 100°C, the intercalate is not ordered for P-100 and P-X-7, as well as HOPG, and an increase in the degree of graphitization decreased the concentration of defects, which hinder desorption. As a result, the activation energy of desorption above 100°C decreased with increasing degree of graphitization. This is probably the basis of the exceptionally good stability reported by others (based on electrical resistivity measurements) for brominated P-100 up to 200°C[2]. Consistent with the resistivity results of ref. 2, this work found through weight measurement that brominated P-100 retains a stable bromine concentration of 17.5 wt.% up to at least 200°C.

A high activation energy of desorption above 100°C is particularly relevant to environmental stability as it pertains to the stability of the more tightly held bromine, which remains after desorption below 100°C is complete. The exceptionally high stability of brominated P-100 is therefore related to the rela-,

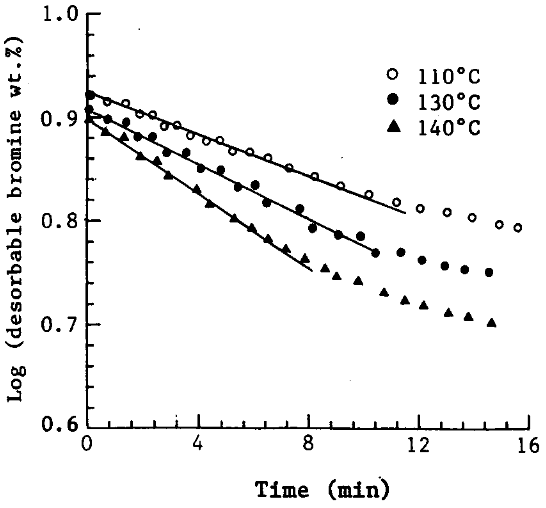


Fig. 10. Logarithm of the desorbable bromine concentration versus time at different constant temperatures above 100°C for brominated P-X-7 fibers.

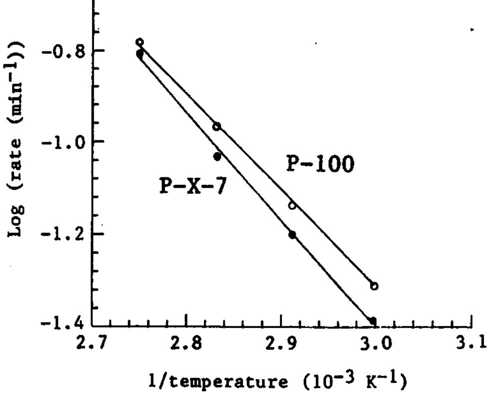


Fig. 11. Arrhenius plot of the desorption rate versus 1/temperature for temperatures below 100°C for brominated P-100 fibers (○) and brominated P-X-7 fibers (●).

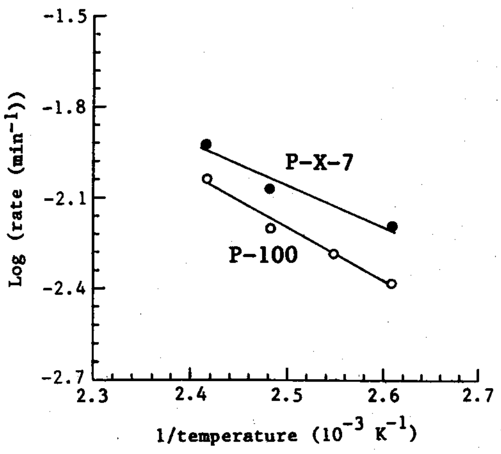


Fig. 12. Arrhenius plot of the desorption rate versus 1/temperature for temperatures above 100°C for brominated P-100 fibers (○) and brominated P-X-7 fibers (●).

tively high activation energy of desorption of brominated P-100 above 100°C. That the activation energy above 100°C increases in the order HOPG, P-X-7, and P-100 is consistent with the report[2] that the thermal stability of the resistivity increases with decreasing degree of graphitization.

The onset of more severe desorption occurs at 100°C during temperature scanning for both brominated P-100 and brominated P-X-7 (Figs. 1 and 2), but the onset is clearer for brominated P-X-7 than for brominated P-100. This is due to the melting of the intercalate in brominated P-X-7 at 100°C and the fact that the intercalate in brominated P-100 is already molten at room temperature[2]. Though less clear, there is still an onset at 100°C for brominated P-100. This is because the chemical state of the bromine intercalate is basically similar in P-100 and P-X-7, as indicated by the intercalate Raman peak around 240 cm^{-1}.

Table 1. Activated energy of desorption from brominated carbon fibers

	Activation energy (kcal/mol Br_2)	
	Below 100°C	Above 100°C
P-100	9	8
P-X-7	12	5
HOPG	17*	4*

*From ref. 6.

Table 2. Stable bromine concentration in brominated carbon fibers

	Stable bromine concentration (wt.%)	
	Below 100°C	Above 100°C
P-100	20	17.5
P-X-7	22	17.5

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