

KINETIC STUDIES OF THE OXIDATION OF HIGHLY ORIENTED PYROLYTIC GRAPHITES

F. RODRIGUEZ-REINOSO*, P. A. THROWER and P. L. WALKER, Jr.
Material Sciences Department, The Pennsylvania State University, University Park,
Pennsylvania, 16802, U.S.A.

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Abstract—Two highly oriented stress-recrystallized pyrolytic graphites have been used to study the kinetics of the carbon-O₂ reaction. Experimental conditions ranged from 700 to 800°C with O₂ pressures from 6 to 60 Torr. Activation energies were determined at 20 Torr O₂ pressure and the order of reaction determined at 725–750°C. Prior to the reaction, specimens were outgassed at about 10⁻⁶ Torr for 8–12 hr at 950°C. The reaction was then followed by continuously monitoring the weight loss using a microbalance. An initial, high transient oxidation rate was shown to be due to surface irregularities at the basal plane edges. Oxidation then occurred at a constant rate (provided that the O₂ pressure was not significantly depleted) with an activation energy of 47–53 kcal/mole, which was shown to be due to the reaction of O₂ with carbon atoms at edges of graphite basal planes. There was no indication of retardation of reaction by concurrent formation of a surface oxygen complex. Reaction order was 0.5 and 0.6 for the two graphites.

1. INTRODUCTION

While there has been general agreement for some time that the oxidation of graphite proceeds at a rate which reflects the general physical anisotropy of the structure, it was not until the optical microscopy studies of Thomas and co-workers[1] that any discrete values could be associated with oxidation kinetics in the basic crystallographic directions. Using naturally occurring single crystals, they studied O₂ attack at the basal plane surfaces from 812°C to 872°C using 10 Torr O₂ pressure. Some slight anisotropy of reactivity was found for the $\langle 1010 \rangle$ and $\langle 1120 \rangle$ directions; but, as would be expected, the largest anisotropy was between attack in the *c* and *a* crystallographic directions. The activation energy for the in-plane reaction was found to be 64 kcal/mole. However, the literature contains values of this

parameter ranging from approximately 35 to 80 kcal/mole[2–11]. These values arise from a number of experiments involving many types of material and a wide variety of temperature/pressure combinations. Consequently, it is difficult to rationalize them to any degree of consistency.

Undoubtedly, one reason for the wide range of values is the varying crystalline perfection and size of the materials used. It is well known that some defects are attacked preferentially and, hence, rapidly expose new sites for reaction. Such a process causes a varying active surface area during the reaction and would be expected to produce spurious results.

What, in principle, is needed to characterize this reaction is a large defect-free single crystal. Since it is not possible to find such a specimen, an approximation to the ideal case has to be made or extrapolated to. The approach here was to use hot pressed pyrolytic graphites of the highest perfections

*Present address: Department of Inorganic Chemistry, University of Granada, Spain.

available*. The materials varied in crystallite size and preferred orientation and contained different densities of crystal defects. It was, consequently, hoped to isolate the effect of these various defects on gasification rates. While the results reported here have not fulfilled the original intention, we feel this work is of intrinsic interest in its own right and, further, it points out in a dramatic way the continuing difficulty of determining kinetic parameters which have fundamental meaning.

2. EXPERIMENTAL

2.1 *Sample preparations*

The two materials used in this study were hot pressed at a temperature of around 3500°C. Consequently, they are highly graphitic. One sample, denoted *M*, had optically flat basal plane surfaces while the other, denoted *P*, had a more irregular wrinkled surface and was not as soft as *M*. The angular spread of the crystallite *c*-axes was 0.5° for *M* and 3.0° for *P*. Cleavage along the basal planes was easy, indicative of highly oriented materials.

Samples of planar dimensions of approximately 2.5 cm by 1 cm were cut from the bulk material using a fine jeweller's saw. Sample thickness varied from 0.05 to 0.20 cm. The edge surfaces were carefully polished using various grades of polishing paper with the final polish being made using tissue paper. In the ultimate polishing stages it was a case of graphite rubbing on graphite so that contamination which might have influenced the oxidation behavior was held to a minimum.

The cutting and polishing actions on such a soft material as graphite produced two features which are probably of importance in interpreting some of the results. First, the smoothly polished surfaces contained loosely

attached graphite particles abraded by the polishing process, as well as containing a significant amount of distorted lattice, that is the basal planes were somewhat deformed at the edges. Second, a lip was produced around the periphery of the basal surfaces. This effect was somewhat reduced by subsequently cleaving the basal surfaces using cellophane tape to remove contamination due to handling during polishing. Cleavage was continued until both basal surfaces were free of any surface steps as far as could be ascertained from optical microscopy studies. By this thickness reduction, the lip height was reduced to an almost insignificant level in both samples.

During the experiment the specimen was held in a cradle formed from two quartz fibers so that no holes needed to be drilled in the specimen for its suspension. The specimen dimensions were carefully measured using a micrometer, a difficult procedure, especially on material *M*, because of its softness. As is discussed later, the important parameter to be derived from the specimen dimensions is geometric edge surface area. The maximum error in this quantity was estimated to be less than 2%.

2.2 *Apparatus*

The graphite samples were suspended by a quartz fiber from a Cahn RG Electrobalance. The signal from the balance was fed to a 1 mV, full scale, Honeywell recorder. The sensitivity of the balance was approximately 10⁻⁶ g. The balance was enclosed in a vacuum system with a double-walled quartz hang-down tube for the specimen suspension. The space between the two walls was continuously evacuated with a mercury diffusion pump to decrease the possibility of diffusion of gaseous impurities into the reaction vessel. The latter was connected to a Vac Ion pump so that it could be evacuated to a vacuum better than 10⁻⁶ Torr during outgassing prior to the reaction. A platinum resistance

*Kindly supplied by Dr. A. Moore of the Union Carbide Corporation, Cleveland, Ohio.

tube furnace provided a uniform hot zone over the sample dimensions, with the temperature being stabilized to $\pm 1^\circ\text{C}$.

The O_2 gas used was "ultrapure" grade supplied by the J. T. Baker Company.

2.3 Procedure

The sample was outgassed at about 10^{-6} Torr for 8–12 hr at 950°C . The temperature was then lowered to that required for the reaction (700 – 800°C) and allowed to stabilize before the desired O_2 pressure was admitted to the system. The activation energy was calculated from an Arrhenius plot of the oxidation rate at various temperatures for 20 Torr O_2 pressure. The order of the reaction was determined by changing the O_2 pressure in the range 6 Torr to 60 Torr at a temperature 750°C for material *M* and 725°C for material *P*.

3. RESULTS

Some typical plots of reaction rate vs time for material *M* are shown in Fig. 1. Figure 2 shows similar plots at the same temperatures for material *P*. In all cases the reaction rate is expressed in micrograms per square centimeter of initial edge surface area (rather than total surface area). The significance and justification for this will become apparent later. It can be seen in Fig. 1 that there is an initially high reaction rate which steadily falls to a constant value. The curves also show a regular change with temperature, with both higher initial and higher ultimate constant rates for higher reaction temperatures. In addition, the time taken to reach the final steady-state rate decreases with increasing reaction temperature. In an isolated run at 650°C , a reaction time of well over 50 hr was required to reach steady-state conditions. In the case of 800°C , the reaction was stopped

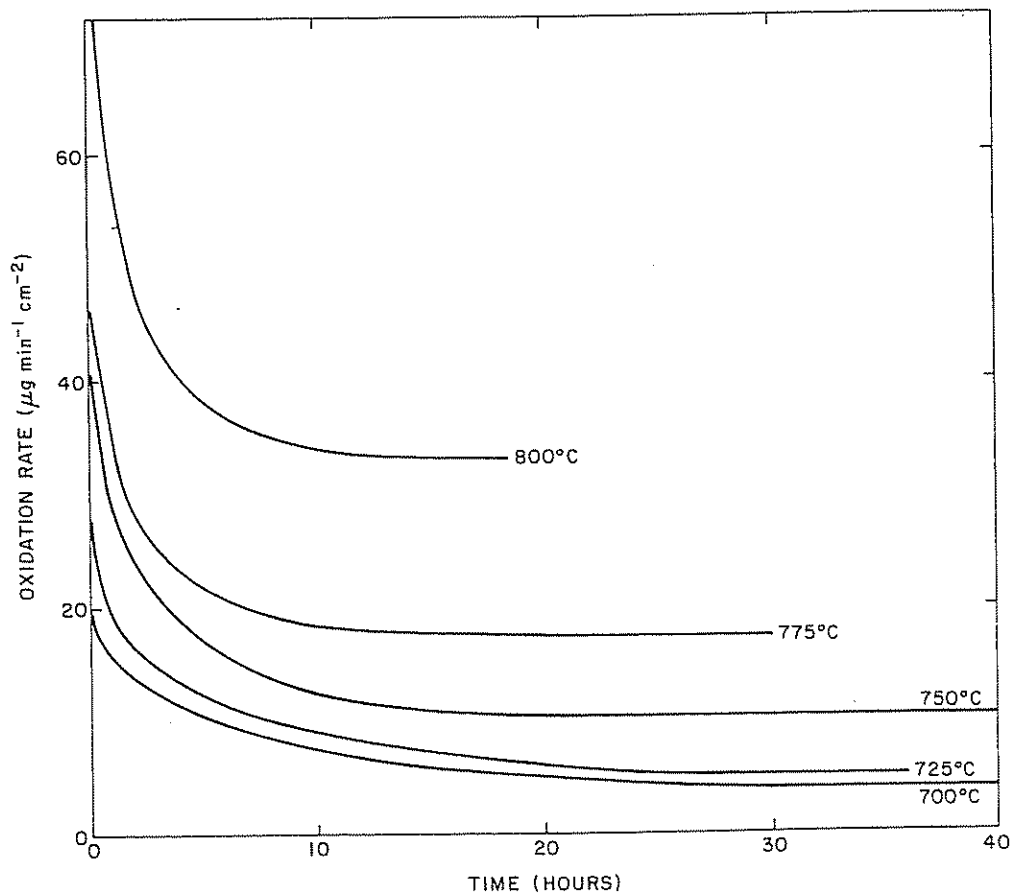


Fig. 1. Variation of reaction rate with time at different temperatures at 20 Torr O_2 pressure for material *M*.

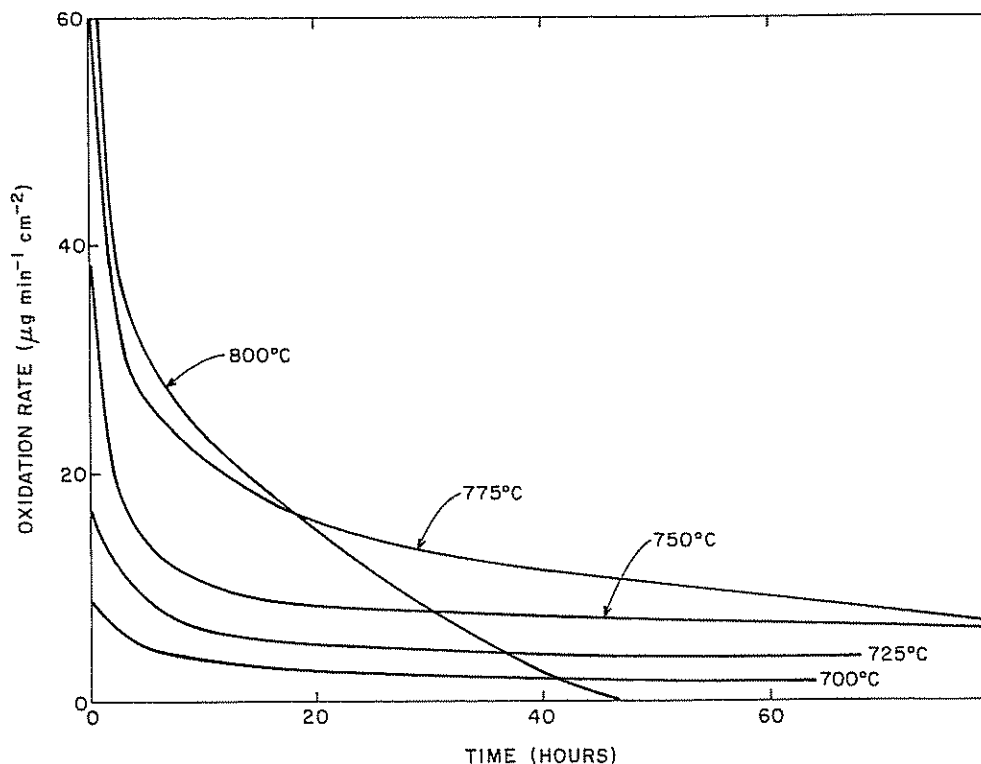


Fig. 2. Variation of reaction rate with time at different temperatures at 20 Torr O_2 pressure of material *P*.

after a few hours at the steady-state rate before significant O_2 depletion took place.

The attainment of the steady-state rate does not correspond to either a fixed per cent burn-off or a fixed weight loss. For sample *M*, constant rates were attained following burn-offs of approximately 4.5%, 2.1%, 3.0%, 2.3 and 2.1% as reaction temperature was decreased in 25°C increments from 800 to 700°C. However, the extra weight loss per unit edge surface area (the edge area varied from sample to sample) in the initial high rate region was approximately constant at each temperature. That is, the areas under the peaks in Fig. 1 are approximately constant between time equals zero and the time at which steady state rates are attained, when the areas due to the steady state rate are subtracted.

For Material *P* (Fig. 2) it can be seen how at lower reaction temperatures (700 and 725°C) the rates decreased from initial high values to steady-state values, which remain constant for the length of the experiment. At higher

temperatures, the oxidation rate decreased continuously and at 800°C stopped when all O_2 in the reaction system was depleted.

Based on the studies of other workers [9-11] a decreasing reaction rate might be attributed to the build-up of a stable surface oxygen complex. In addition, the gradual depletion of O_2 accompanied by the build-up of gaseous reaction products might also inhibit the reaction. To test for these possibilities, several samples were outgassed for 8 hr at 950°C to a final pressure of 2×10^{-6} Torr after the steady-state had been attained. Under these conditions, stable oxygen complex which had formed under reaction conditions would be removed as CO and/or CO_2 [9]. A fresh charge of O_2 , at a pressure of 20 Torr, was then admitted to the reaction vessel at the previous reaction temperature. With material *M*, in all cases, the new reaction rate coincided with the earlier steady-state rate and continued at this rate for as long as the reaction was observed, generally around 10 hr. This indicates that the fall in

reaction rate to a constant value was not, in this case, due to the build-up of a stable oxygen complex, depletion of O_2 , or build-up of gaseous reaction products. In the case of material *P*, the behavior was the same at the lower temperatures (700 and 725°C) as that found for material *M*. However, at higher temperatures there were some differences. That is, when a fresh dose of O_2 was admitted to the system, the reaction proceeded at a constant rate for some period, but at a higher rate than at the end of the initial reaction. Significant depletion of O_2 during the initial reaction runs at the higher temperatures had occurred.

The time taken for the complete cessation of the reaction of material *P* at 800°C was inversely proportional to the specimen area since the specimen perimeter was always within a few per cent of a constant value) as seen in Fig. 3. That is, the rate plotted vs the

product of time and thickness gives a common curve for six samples. The ratio of basal plane surface to edge surface for the samples ranged from 4.4 to 12.9. These results indicate that O_2 attack on these samples occurred predominantly at the edge surface.

The high crystallite alignment in the materials used in these experiments offered a unique possibility of evaluating separately the reactions on edge and basal surfaces. Several samples of *M* which had been burned off to the region of constant reaction rate were cleaved so that all traces of oxygen attack had been removed from the basal plane surfaces. The specimens then had fresh basal surfaces of areas closely approximating the original basal area. By contrast, the previously reacted edge surfaces were decreased in area in direct proportion to the decrease in sample thickness. The thinned samples were then reacted with a fresh charge of O_2 at the

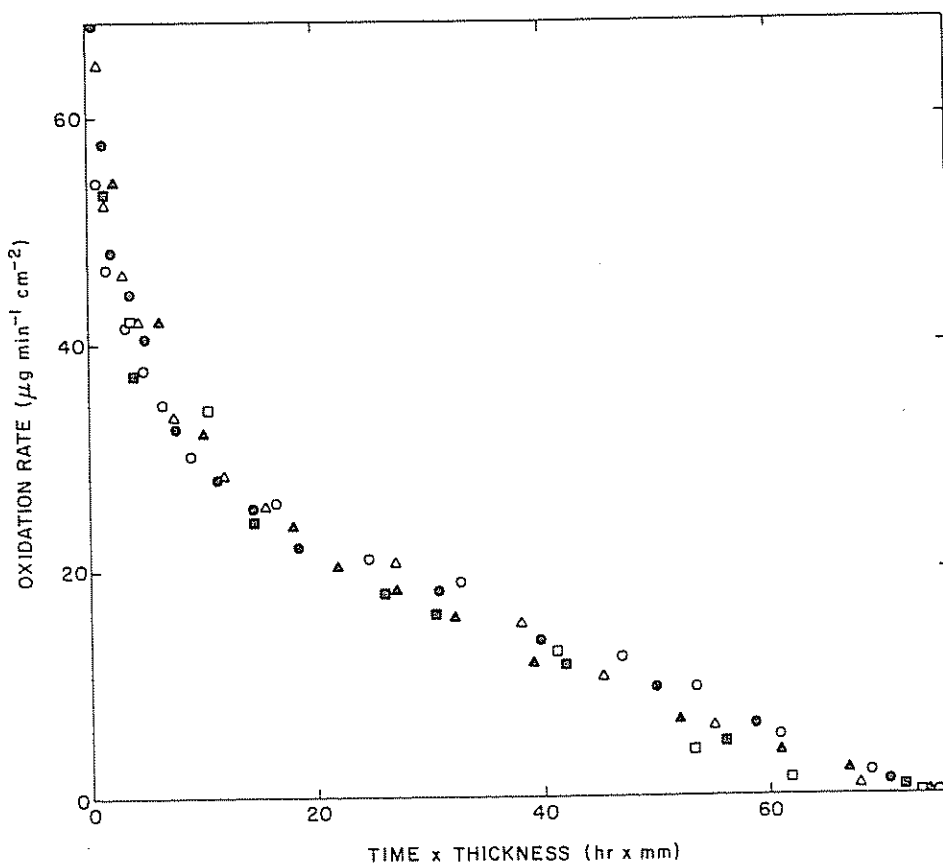


Fig. 3. Variation of reaction rate with product of time and thickness of material *P* at 800°C. Six samples reacted.

same temperature and pressure. In each case, the effect was as shown by the dashed curve in Fig. 4. That is, the reaction continued, following a slight initial peak, at the same constant rate as the rate found at the end of the first run. This is true only if the reaction rate is expressed as weight loss per unit of edge surface area rather than total surface area. This indicates that the true edge oxidation rate was constant after the initial decrease in the first run and that basal plane attack was insignificant as far as its contribution to the weight loss was concerned. Optical microscopy examination[12] indicated that the slight initial peak found during reaction of the cleaved samples can be attributed to preferential oxidation of nonbasal defects. The pits produced then expanded at a rate common to that of the edge surface, thus making a small contribution to the edge erosion rate.

The high reaction rate at the beginning of an experiment on a polished sample is, therefore, not due to reaction at basal surfaces but rather at edge surfaces. It is suggested that the cause of this large initial rate is related to the condition of edge surface after polishing. To prove this, a sample oxidized to a steady-state rate was cleaved at both basal surfaces, repolished on two orthogonal edge

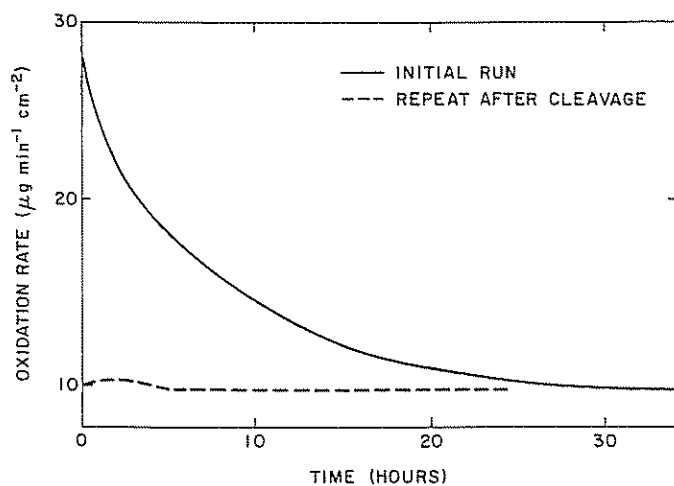


Fig. 4. Comparison of reaction rate at 750°C of an original piece of material *M* with rate on a cleaved sample following the initial reaction. Rates normalized to per unit geometric edge area.

surfaces, and reoxidized at the same temperature and pressure. An initial high rate resulted which fell midway between the initial rate and the steady-state rate for the original sample.

The activation energy for the reaction, in the case of material *M*, was calculated using the steady-state rate since this appears to be the true indicator of reaction rate parallel to the basal plane. An Arrhenius plot of reaction rate as a function of temperature is shown in Fig. 5. The value obtained, 47 ± 3 kcal/mole, is in good agreement with the values of Hennig[3] and Laine *et al.*[9], but reported values vary widely above and below this value. For material *P*, the activation energy was calculated using the steady-state values reached after every sample had been outgassed and a new dose of O_2 admitted. An Arrhenius plot is also shown in Fig. 5. The value of 53 ± 3 kcal/mole is in good agreement with material *M*.

Several experiments were performed to determine the dependence of rate on O_2

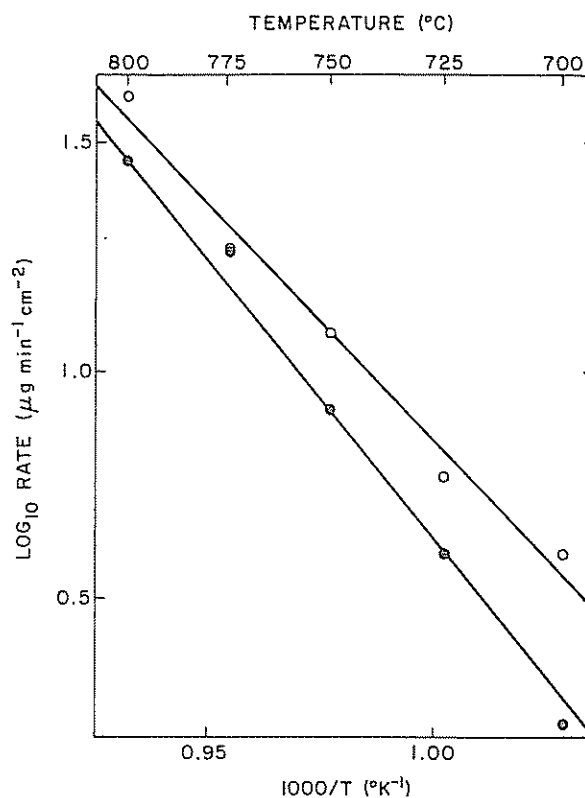


Fig. 5. Arrhenius plots of steady-state reaction rates for materials *M* (○) and *P* (⊙).

pressure for the two graphites, following initial burn-off of the *M* and *P* samples at 750°C and 725°C, respectively, to attain a constant rate. The pressure was decreased in at least five increments from 60 to 6 Torr, with a constant rate at each pressure being quickly established. In the expression, rate proportional to $P_{O_2}^n$, $n=0.6$ and 0.5 for the *M* and *P* materials, respectively. The values were reproducible over a number of cycles.

4. DISCUSSION

The experimental results presented above have allowed for a logical approach to determining the cause of the initial transient high reaction rate in these experiments. That it appears to be connected with the polishing procedure indicates three possible explanations, any combination of which may be important. The first two are related to the effects of cutting and polishing referred to earlier, i.e. the edge lip and surface deformation; both of these may contain more reactive material. In addition, it is possible that impurity particles, which have a catalytic effect, were picked up during the polishing process. In both materials, some evidence of possible catalytic activity was visible from scanning electron microscope (SEM) studies[12]. Channels of enhanced activity originating at the edges of the sample were clearly observed, but they showed no signs of a catalyst particle at their terminations as is common in such cases. This would indicate that the activity of the catalyst was itself possibly destroyed by oxidation and that the catalyst was active only during a very limited time, that is during the initial high reaction rate period. Such results have been reported previously, when iron is used as a catalyst, for example[1]. SEM studies[12] reveal that in material *P* the channels are much deeper than in material *M*, in some cases up to two-thirds of the sample thickness.

Of particular significance in this study is the finding that constant reaction rates ex-

pressed as weight loss per unit reaction time per unit starting geometric edge area can be attained following an initial sharp decrease in rate. That is, the rate is independent of basal plane area but directly dependent upon edge area, indicating that a high anisotropy of rate of attack by O_2 existed in the different crystallographic directions. In a future paper, the consequences of this on the measured rates of recession of highly oriented pyrolytic graphites in essentially the *c* and *a* crystallographic directions will be reported.

From Fig. 5 is seen that over the temperature range studied the steady-state reaction rate for material *P* is lower than that for material *M*. At least one reason for this is apparent from microscopic studies of the edge surfaces[12] which reveal that the edge of *M* is rougher than the edge of *P*. The reason(s) why upon oxidation the *M* material developed a rougher edge surface is not understood at this time, but the rate expressed per unit geometric edge area would be reduced more for material *M* than for material *P*.

The activation energy for the C- O_2 reaction obtained for the materials studied is well defined in that the results are very reproducible. The question then arises as to whether the activation energy is dependent on the characteristics of the specimen since there is such a wide range of published values. These well oriented materials give values in good agreement with that found by Hennig[3] using natural graphite single crystals. Single crystals are similar in many properties to the material used here. However, it is evident that values around 50 kcal/mole are not solely characteristic of a highly oriented single crystal-type material. That is, Thomas *et al.*[1] obtained a much higher value from their studies on the rates of etch pit enlargement in Ticonderoga crystals. On the other hand, Laine *et al.*[9] obtained a value similar to ours using a graphitized carbon black, Graphon.

Evans *et al.*[4] have also obtained different

values for activation energies depending on the depth of the expanding pits they observed. Using the etch decoration technique, they observed the growth of monolayer pits and obtained a value of 35 kcal/mole; whereas the expansion of deeper pits, observed by optical microscopy, gave a mean value of 64 kcal/mole [1]. Hennig, using the etch decoration technique, reported a value of 97 kcal/mole [2] for the carbon-air reaction. Baker has recently observed oxidation of single crystals in the electron microscope using a controlled oxidation technique. The rate was measured by recording the recession of surface steps. An activation energy of 51 kcal/mole was obtained, which is also in good agreement with the values obtained here.

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