

## LETTERS TO THE EDITOR

Transient Rates in the Reaction of CO<sub>2</sub> with Highly Oriented Pyrolytic Graphite

(Received 10 June 1974)

Transient gasification rates in the reaction of CO<sub>2</sub> with spectroscopically pure natural graphite have been shown by Shelef and Walker[1] to be closely related to the purity of the reacting system. In particular, hydrogen and hydrogen-containing gases prevent the occurrence of high transient rates, apparently through chemisorption on active sites involved in transient gasification. Even in highly purified CO<sub>2</sub>, vigorous outgassing conditions were needed to produce high rate transients. Shelef and Walker proposed that the kinetics of transient gasification could be explained by a model involving two kinds of surface oxides differing in reactivity. The more reactive oxide is responsible for the high initial rate. The decay of the transient to a steady-state value was postulated to occur through the transition of the more reactive oxide into a stable type.

This same transient phenomenon has been examined by us using highly oriented, compression-annealed pyrolytic graphites, supplied by the Carbon Products Division of Union Carbide Corporation. The characterization of these graphites, using X-ray diffraction and O<sub>2</sub> etching, has been reported on in detail elsewhere [2, 3]. Samples were cut into parallelepiped sections, the basal surfaces were cleaved with cellophane tape, and the sample edges were polished with very fine emery paper. The polishing served to eliminate much of the roughness introduced during the cutting process[4]. Before reaction with CO<sub>2</sub>, samples were oxidized in O<sub>2</sub> (to about 2 per cent burn-off) to further eliminate any loose or disordered material[4] and then were outgassed under a vacuum of about  $5 \times 10^{-6}$  Torr. Reactions were carried out at about 50 Torr CO<sub>2</sub> pressure and at temperatures of 1050 and 1100°C. 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. More details on the apparatus are given elsewhere[4]. The CO<sub>2</sub> used was research grade, supplied by Matheson Products. It had a guaranteed purity > 99.995 per cent.

Figure 1 shows the results of three consecutive runs made with a single specimen pre-oxidized to 2.3 per cent burn-off. The peak rates are seen to decrease progressively with burn-off. The steady-state rate is the same for the three runs as cumulative burn-off increased from 2.3 to about 6 per cent. In the third run, the transient is barely discernible, in spite of the longer outgassing time. It is also interesting that the outgassing conditions employed in runs 1 and 2 were somewhat less severe than those used by Shelef and Walker (> 10 hr at 1100°C).

The results of Fig. 1 suggest that active sites involved in the transient regime are gradually eliminated with burn-off and that the decay of the transient is, in part, due to sample burn-off. On the other hand, if burn-off were the only factor affecting transient decay, then a second transient would not have materialized (run 2).

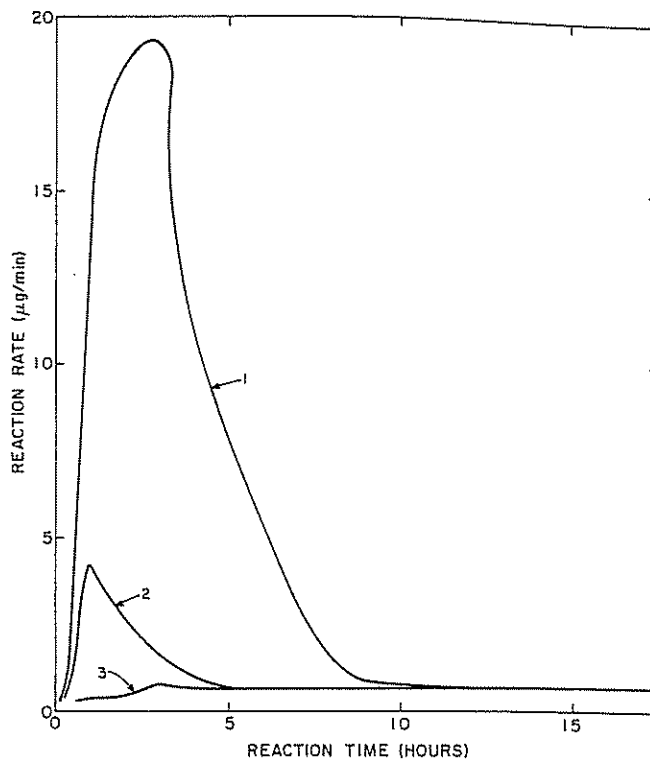


Fig. 1. Change of reaction rate with reaction time at 1050°C for three consecutive runs. Prior to each gasification run sample outgassed at 1075°C for 4 hr (runs 1 and 2) and 12 hr (run 3).

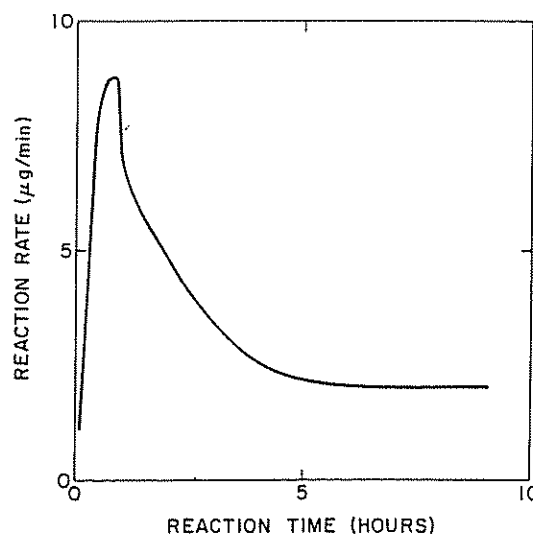


Fig. 2. Change of reaction rate with reaction time at 1100°C for sample previously reacted as shown in Fig. 1. Prior to gasification sample outgassed at 1075°C for 4 hr.

A second run, using the same outgassing and reaction conditions, was also made with a sample that had been pre-oxidized in O<sub>2</sub> to about 50 per cent burn-off. As expected, no rate transient was observed. In order to evaluate the possible influence of catalytic impurities conceivably introduced during sample cleavage and polishing, a run was made with a sample that had been heat-treated at 2500°C in a flowing argon stream. This sample was also pre-oxidized in O<sub>2</sub> to about 50 per cent burn-off. Again no rate transient was observed.

To examine the influence of reaction temperature, a run was then made at 1100°C using the same sample described in Fig. 1. As is seen in Fig. 2, a pronounced transient rate reappears with a peak value which is intermediate between those for runs 1 and 2 at 1050°C. The combined results of Figs. 1 and 2 indicate that the active sites involved in transient gasification may be structurally different at different temperatures. From the steady-state rates at 1050 and 1100°C, an activation energy of 81 kcal/mole is calculated

for the C-CO<sub>2</sub> reaction. This is in good agreement with over-all activation energies previously reported for this reaction[5].

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### Coking Yield and the Acidity of Carbon Black†

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For a series of experimental graphites made with various concentrations of a fine channel black (Carbolac 1, Cabot Corporation) dispersed in a coal-tar pitch, we observed that the *in-situ* binder-coking value increased as the concentration of channel black increased. This behavior is shown in Fig. 1. When

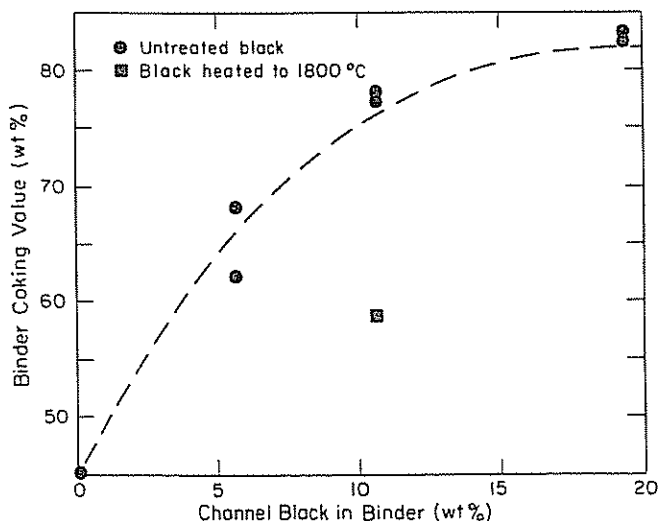


Fig. 1. Binder coking value in experimental graphites vs concentration of channel black in the coal-tar pitch binder.

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another graphite was made containing a sample of channel black that had been heated to 1800°C, the coking value dropped from 78 to 58 per cent (Fig. 1). In a similar experiment, where the channel black was replaced with a thermal black (Thermax, Theratomic Carbon Company), we did not observe a similar effect, regardless of heat-treatment of the black. These results can be understood by observing the changes in the acidity of the carbon blacks that occur on heating. By measuring the pH of water slurries containing 1.2 g of carbon black in 100 ml of water, for both the as-received and heated (1800°C) materials, we arrived at the results in Table 1. Also included in the table are the volatiles lost on heating. In the as-received condition, the thermal black is only slightly acidic (pH 6.6), and is essentially unchanged after heating. The channel black, however, is very acidic (pH 3.4) to start with, but becomes quite basic (pH 10.4) after heating. Evidently, this black contains acid forming materials, groups or complexes, which are destroyed irreversibly when heated. Small amounts of alkaline salts remain after heating and lead to the basic nature of the carbon black.

Acidic conditions promote the coupling of the aromatic molecules of the pitch. Following is a reaction sequence by which

Table 1. Acidity of carbon blacks

Black	Acidity <sup>a</sup> (pH)		Volatiles <sup>b</sup> (%)
	As-Received	Heated <sup>b</sup>	
Channel	3.4	10.4	24
Thermal	6.6	6.4	0.7

<sup>a</sup>These pH values were determined immediately after slurrying. Because of the low buffer capacity of the slurry containing channel black, we subsequently found that its pH values stabilized at 3.7 and 6.7 for the as-received and heated conditions, respectively.

<sup>b</sup>At 1800°C.