er, two alternative explanations exist. One, which appears unlikely from the recent work of Parks *et al.* (28), is that the unchanged nitrogen oxides enter the bloodstream and react with hemoglobin to form a nitrogen oxide-iron complex (29). Alternatively, our data (30) as well as the *in vivo* data of Thomas *et al.* (9) show that NO_2 initiates lipid peroxidation even in aqueous systems. Addition of NO_2 would produce a lipid-bound nitro group; however, the hydrogen abstraction mechanism suggested here converts NO_2 to nitrite ions that would be carried throughout the body, as shown by Goldstein *et al.* (27).

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10 November 1980; revised 3 June 1981

Mechanism of Single-Layer Graphite Oxidation: Evaluation by Electron Microscopy

Abstract. *Etch-decoration reveals that the rate of removal of carbon atoms exposed at monolayer steps on graphite surfaces depends on the population density of these edge atoms (the rate is higher at a low-density surface) and that carbon removal continues for a prolonged period after the oxygen supply in the gas phase has been shut off. The edge carbons are removed by both oxygen from the gas phase and oxygen in the adsorbed oxides which migrate from the neighboring basal carbon atoms.*

The first step in all gas-solid and solid-catalyzed reactions is the adsorption of the gaseous molecules on the solid surface. It is known that only on specific active surface sites can the adsorbed molecules react to form products, which may then desorb to the gas phase. This general class of reaction mechanism is known as the Langmuir-Hinshelwood (LH) mechanism, which has been a cornerstone model in catalysis and heterogeneous kinetics. The Michaelis-Menten mechanism for enzymatic reactions is synonymous with this mechanism. More recently, information on the mobility of the adsorbed species on the surface has been accumulating. A fundamental question, consequently, is how the mobile adsorbed species participates in the reaction. This question has been challenging enough that numerous indirect evidence for such a mechanism has been published (1). Along this line, we have measured the rate of removal of carbon atoms by oxygen on the monolayer steps on graphite, which are the active sites. We have found that the rate of removal, in atoms per active site per second, depends to a large extent on the population density of the active sites; the rate declines as the population density of these sites increases and carbon removal continues for a prolonged period after the O_2 supply in the gas phase has been cut off. The number of nonactive carbon sites was much greater than the number of active sites (by about 10^5 to 10^8). Our results show that the carbon at an active site is removed by two mechanisms: (i) direct reaction with O_2 in the gas phase or the LH mechanism and (ii) reaction with the migrating oxygen atoms of the surface oxides which are first dissociatively chemisorbed on the nonactive sites.

The experimental technique consists of etch-decoration followed by examination with transmission electron microscopy (TEM). The technique. described elsewhere (2), consists of cleaving single crystals (natural graphite from Ticonderoga, New York) to a thickness of a few hundred angstroms, etching the graphite in a gas (in our case, 20 percent O_2 in argon at 1 atm) which expands the surface vacancy to create a pit one atomic layer deep, decorating the edge of the pit with gold nuclei, and examining with TEM. The radius of the pit is proportional to the time of etching. The atoms on the edge of the pit are the active sites. From the pit growth rate, we are able to calculate the rate of removal of carbon atoms per active site.

The reaction with O_2 starts from the residual vacancies present on the basal surface. The density of the natural vacancies can be counted as the ring densi-

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ty on the electron micrograph. In counting the ring densities, we examined at least 200 rings to obtain a statistically meaningful figure. In about 500 etch-decorated samples that we have examined, the vacancy densities ranged from 0.1 to 60 μm^{-2}. Typical results of the ring growth rate, as the ring size after 20-minute etching, are shown in Figs. 1 and 2. The three points (A, B, and C) in Fig. 2 correspond to the micrographs in Fig. 1. Examples of the rates calculated from Fig. 2 are 0.6 carbon atoms removed per carbon atom per second for a vacancy density of 10 μm^{-2} and 0.9 carbon atoms removed per carbon atom per second for a vacancy density of 1 μm^{-2}. The rate levels off to 0.5 carbon atoms removed per carbon atom per second for surfaces with high vacancy densities. Furthermore, carbon removal continues after the O_2 is shut off and the crystals are flushed in argon at the etching temperature. This phenomenon is more enhanced for surfaces with lower vacancy densities (Fig. 3). The ring growth during this period shows preferential directions, which results in noncircular shapes. Reaction during the flushing period is due to the surface oxides which migrate on the basal plane to the edge carbon atoms.

Of the two independent rate processes that contribute to the reaction between carbon and oxygen, only the reaction with the migrated oxides that are first chemisorbed on the nonactive sites is influenced by the population density of the active sites because the nonactive sites are shared as the collecting sites for oxides. The contribution by the surface migration mechanism to the overall rate can be substantial for the carbon-oxygen reaction. Furthermore, our new technique of flushing with an inert gas can yield values for chemisorption and the surface diffusion coefficient at elevated temperatures. For the carbon-oxygen reaction at 650°C, these values are oxygen adsorbed on carbon = 0.34 (from 14-hour flush data) and surface diffusion coefficient = 5×10^{-12} cm^2 sec^{-1} for an initial vacancy density of 1 μm^{-2}; for an initial vacancy density of 10 μm^{-2}, the corresponding values are 0.06 and 2 × 10^{-12} cm^2 sec^{-1} (3).

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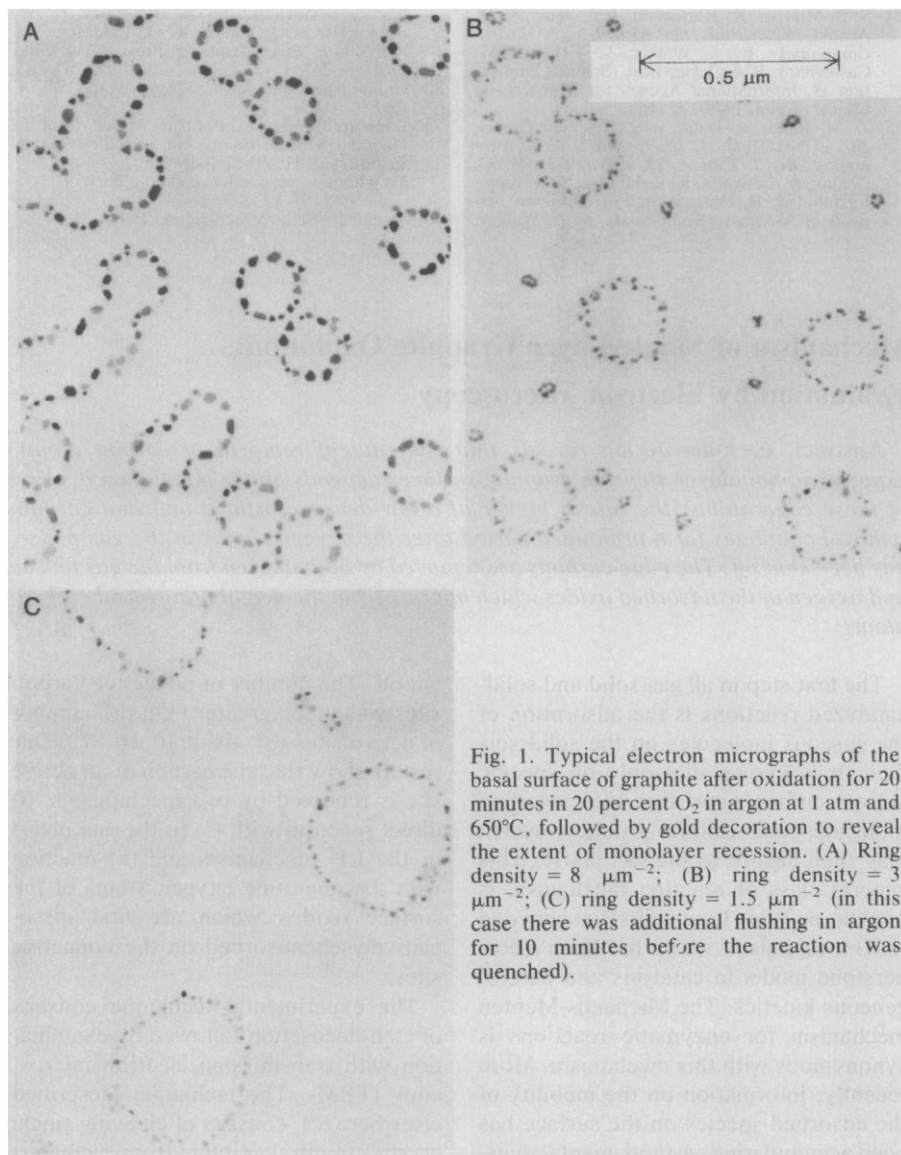State University of New York at
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Fig. 1. Typical electron micrographs of the basal surface of graphite after oxidation for 20 minutes in 20 percent O_2 in argon at 1 atm and 650°C, followed by gold decoration to reveal the extent of monolayer recession. (A) Ring density = 8 μm^{-2}; (B) ring density = 3 μm^{-2}; (C) ring density = 1.5 μm^{-2} (in this case there was additional flushing in argon for 10 minutes before the reaction was quenched).
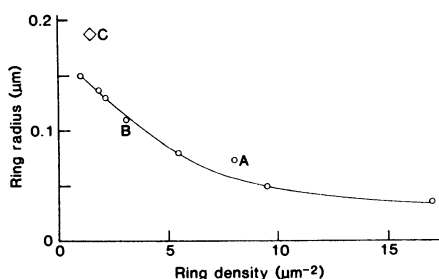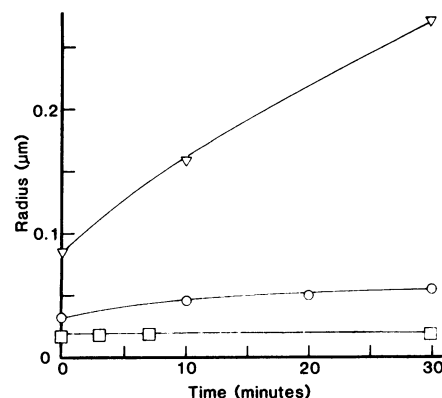

Fig. 2 (left). Dependence of the ring size, which is proportional to the rate of carbon removal, on ring density. Fig. 3 (right). Ring radii versus time of flushing in argon after 10 minutes reaction in 0.2 atm O_2 (0.8 atm argon) at 650°C. Ring density = 1 μm^{-2} (∇), 10 μm^{-2} (○), and > 20 μm^{-2} (□). Zero time corresponds to the time when the O_2 supply is cut off.

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20 March 1981; revised 15 July 1981