

## "Kinetics of Oxygen Chemisorption by Graphon"

The first step in the reaction of oxygen with carbon is the fixation of oxygen to certain active sites on the carbon surface to form surface oxides. A mass spectrometric study of the reaction was performed to delineate the role of surface oxygen compounds in the reaction of oxygen with Graphon, a highly graphitized carbon black. Samples of Graphon were activated to nine different levels by oxidation to burn-off levels of zero to 35 percent. These samples were reacted with oxygen in a static reactor at temperatures between 450 and 675°C with initial oxygen pressures varying from 6 to 73 millitorr.

The surface of activated Graphon was found to be composed of groups of active sites with differing reactivities. The active surface areas of the samples were determined by chemisorption of oxygen and also calculated from the reactivity data. The chemisorptions were performed in the static system for twenty-four hours from an initial oxygen pressure of 0.5 torr at temperatures between 300 and 550°C. The amount chemisorbed did not increase significantly in the temperature range 300 to 450°C. However, between 450 and 550°C the amount chemisorbed increased sharply.

The active surface area estimated from the low surface coverage data using an integrated form of the rate law was found to be in substantial agreement with the coverage attained by chemisorption in twenty-four hours at 300°C from an initial oxygen pressure of 0.5 torr. This value had previously been shown to be an index to the reactivity of activated Graphon samples.

The rate law that best described the data at low surface coverages was found to depend upon the oxygen pressure and the active surface area available for reaction. It was determined that the reaction was first order with respect to oxygen pressure. The effect of surface coverage was best described by the distribution of surface oxides expected for a dissociative, mobile adsorption of oxygen. At higher surface coverages the rate followed a more complex law.

The rate law on the most active Group of sites was given as

$$-R_{O_2} = k_{O_2} P_{O_2} TAS(1) [1 - \theta(1)]^2$$

where  $TAS(1)$  is the total surface area covered by the most active sites and  $\theta(1)$  is the fraction of these sites covered with oxide. The rate constant was found to be  $1.6 \times 10^5 \text{ cm sec}^{-1} \exp(29 + 2 \times 10^3/RT)$ . The experimental entropy of activation was calculated to be -21 e.u. Comparison with theoretical entropy changes showed this value to be of the order expected for the formation of a mobile transition state complex leading to chemisorption of oxygen. The mechanism presented for the

chemisorption of oxygen onto this most active group of sites was (1) the formation of a mobile transition state complex composed of one oxygen molecule and two adjacent surface sites and (2) the dissociation of the oxygen molecule on the surface to form two mobile surface complexes each composed of one oxygen atom and one surface site.

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