

The formation of surface oxide by carbons during
oxidation by atomic oxygen at different temperatures.

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The reaction of atomic oxygen with carbons and graphite has been reported variously as temperature dependent and temperature independent. Such discrepancies are probably due to large variations in experimental techniques. Otterbein and Bonnetain (C.R. Acad.Sci., 1964, 258, 2563; 259, 791) found the reaction to be temperature dependent and interpreted their results in terms of inhibition of the reaction at low temperatures by surface oxide formed during reaction at low temperatures (25°-100°C). Above 100°C there was a marked increase in reaction rate to about 150°C, the reaction rate thereafter levelling off and becoming almost independent of temperature (150°-700°C). This present study has been designed to test further the temperature dependence of the reaction and to measure the amounts of surface oxide formed with increasing temperature. Carbon prepared by carbonisation of polyvinylidene chloride (1300°C) and graphite crystals have been oxidised in the temperature range 20°-350°C by atomic oxygen formed from molecular oxygen in a low-pressure, flow apparatus utilising a microwave discharge. Rates of oxidation were obtained utilising a micro-electromagnetic vacuum balance. Extents of surface oxide formation were measured by outgassing in vacuum over selected temperature intervals, collecting the desorbed gases and analysing in a mass spectrometer. Small amounts of carbon (40 milligram) were oxidised in an attempt to ensure that excess of atomic oxygen was flowing over the carbon. When oxygen containing nitrogen as a trace impurity is passed through a microwave discharge the nitrogen is converted to nitric oxide. This nitric oxide was found to be adsorbed by the carbon sample during the course of reactions carried out at temperatures below 100°C. Most of the nitric oxide (90%) was desorbed in vacuum at 100°C, the remainder leaving the surface on heating to 200°C. The effect of nitric oxide cannot be ignored as it could act as an inhibitor by poisoning the surface and by promoting recombination of atomic oxygen. To avoid these effects oxygen, free from nitrogen, prepared by thermal decomposition of potassium permanganate was used in subsequent experiments. The removal of nitrogen at the same time affected the mechanism of atomic oxygen production in the microwave discharge resulting in lower concentrations. Using this purified oxygen the oxidation reaction was again found to be temperature dependent in agreement with previous results from these laboratories. Equilibrium quantities of surface oxide decreased continuously with increasing reaction temperatures. Of the surface oxide formed at 25°C, 15% desorbed on heating to 100°C, with a further 45% from 100°-200°C. The percentage of carbon dioxide in the desorbed gases decreased with increasing outgassing temperature. The amounts of surface oxide formed at reaction temperature of 100°C and above were relatively small to those formed at 25°C. These results are discussed in terms of the conclusions of Bonnetain and in terms of mechanisms of gasification.