

The Role of the Surface Complex in the Kinetics of the Reaction of Oxygen with Carbon

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Abstract. Using thin films of pyrolytic carbon the kinetics of the reaction with oxygen were studied in a static system over the temperature range 748-1173 K at pressures in the neighborhood of 1 Torr (0.13 kPa). The formation of the stable surface complex, measured by pressure change and by temperature-programmed desorption, and products carbon monoxide and carbon dioxide were monitored as a function of reaction time during the complete course of the reaction. At lower temperatures an induction period was observed for formation of carbon monoxide and carbon dioxide but not for formation of the complex. The presence of the complex on the surface before the start of a reaction shortened the induction period and increased slightly the over-all rate. A mechanism for the reaction is proposed in which the surface complex is an intermediate in the formation of carbon monoxide and carbon dioxide.

Introduction

Of central importance in the processes occurring on the surface of carbon during the reaction with oxygen is the presence of the strongly-bound complex formed by adsorption of oxygen on carbon (1). Although its properties have been studied by various techniques its role in the oxidation process has been difficult to define. The purpose of the present work was, by a careful measurement of the time course of the reaction under a variety of conditions, to describe the mechanism of the oxidation and the role of the complex in it.

Experimental

The reaction was studied in a static system containing a reaction vessel connected to two pressure transducers. Thin films of high purity carbon (15 nm thickness) were deposited on the surface of the vessel by pyrolysis of 40 Torr (5.3 kPa) of methane at 1223 K. The amount of carbon in the film was measured by the attenuation of a He-Ne laser beam passed axially through the vessel.

Results

Measurement of the Active Surface Area (ASA)

After a degassing treatment of the film, 300 Torr (40 kPa) of oxygen was admitted to the vessel at 673 K, allowed to chemisorb for about 15 hours and removed by evacuation to a pressure of 10^{-5} Torr (10^{-6} kPa). The temperature of the furnace was

linearly programmed at 5°/min. from 673-1223 K and desorption of carbon monoxide was measured by the increase in pressure in the system. During the desorption the product carbon dioxide was removed by trapping and at the end of the desorption both products were analyzed. The ASA of the carbon films was a reproducible measurement and varied from about 1% of the total amount of carbon for new films to about 10% of the total carbon for a film after 80% reaction. From the temperature at the maximum rate of desorption an activation energy for desorption was estimated as 290 kJ mol⁻¹.

Kinetic Measurements

The time course of the reaction with oxygen at pressures in the region of 1 Torr (0.13 kPa) was followed by monitoring the concentration of carbon on the surface and the pressure in the reaction vessel and was measured over the temperature range 748-1173 K.

(a) 748-923 K

Below about 898 K carbon monoxide was less than 1% of the carbon dioxide in the products. Under these conditions the loss of carbon may be equated to the carbon dioxide produced. The pressure will equal the sum of the oxygen plus carbon dioxide and a decrease in pressure will indicate loss of oxygen by adsorption on the surface, which in the present experiments we have equated to formation of the stable complex. An example of the time course of the reaction with respect to formation of complex and of carbon dioxide is shown in Figure 1. Note

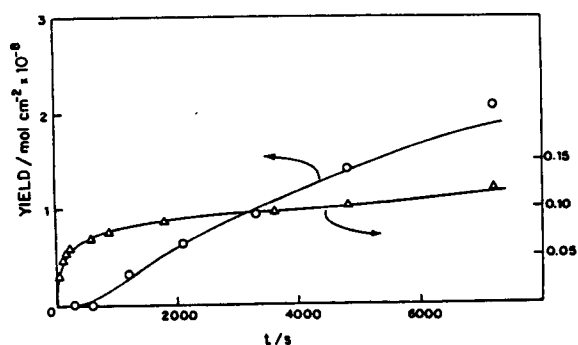


Figure 1. Yields of complex and of carbon dioxide as a function of time. Pressure of $O_2 = 1$ Torr (0.13 kPa). $T = 848$ K.
 \circ — CO_2
 \triangle — complex

that the scale for formation of the complex is ten times larger than for the formation of carbon dioxide. At each temperature it was clearly observed that formation of carbon dioxide involved an induction period (60 min. at 748 K to 2 min. at 900 K) while no induction period was observed for formation of the adsorbed oxygen, or stable complex. The initial rate of formation of the complex was measured at each temperature. An Arrhenius plot of this rate, normalized with respect to the initial pressure of oxygen, gave an activation energy for adsorption of 46 kJ mol^{-1} .

(b) 923–1173 K

At higher temperatures the induction period was much shorter and initial rates of disappearance of carbon and of formation of products were more easily defined. At 998 K carbon monoxide was no longer negligible and in the initial stages amounted to about 25% of the carbon dioxide. As carbon monoxide accumulated in the products the secondary reaction with oxygen became important and the ratio CO/CO_2 fell with increasing conversion. The product ratio CO/CO_2 is therefore significant only at low conversion.

In the high temperature region the decrease in pressure caused by the formation of complex was negligible compared to the increase caused by the production of carbon monoxide. The rate of removal of carbon can therefore be equated to the rate of formation of $CO_2 + CO$.

The activation energy for formation of carbon monoxide, $\sim 300 \text{ kJ mol}^{-1}$, is about the value expected for desorption of the stable surface complex, whereas the activation energies for removal of carbon, $\sim 170 \text{ kJ mol}^{-1}$, and for formation of carbon dioxide, $\sim 130 \text{ kJ mol}^{-1}$, are considerably lower.

The Product Ratio CO/CO_2

The ratio of the products CO/CO_2 , measured in the initial stages of the reaction, is shown in an Arrhenius plot in Figure 2. The circles represent either new films or films from which the complex was removed by TPD after reaction. The squares represent films from which the complex was not removed and was therefore present on the surface at the beginning of the reaction. From the slope of this plot a value for ΔE , the difference in activation energy for the rates of formation of carbon monoxide and carbon dioxide, was 192 kJ mol^{-1} . This is in agreement with the difference deduced

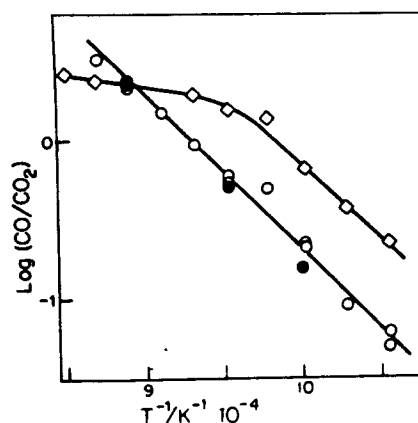


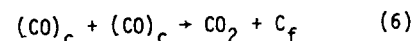
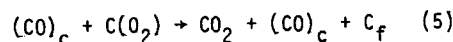
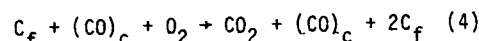
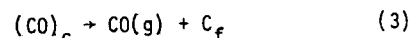
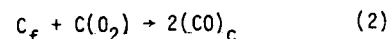
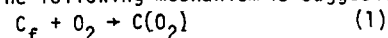
Figure 2. Arrhenius plot of the ratio CO/CO_2 in the initial stages of the reaction.

- \circ — new films
- \bullet — films from which the complex had been removed
- \diamond — films from which the complex had not been removed

from the separate measurements of the rates. Below about 1048 K, the ratio CO/CO_2 from films from which the complex was not removed was about three times larger than observed from new films. The difference in activation energy was, however, the same as observed for the new films. At temperatures above about 1048 K the ratio decreased and gradually reached the value observed for new films. This trend is explained by the fact that at higher temperatures the equilibrium amount of complex on the surface becomes very small and its effect on the reactions is correspondingly reduced.

Discussion

The yield-time curves obtained in the low-temperature region clearly show that adsorption of oxygen on the carbon surface, as measured by the decrease in pressure, is a primary process, while formation of the product carbon dioxide is a secondary process. The following mechanism is suggested:



where C_f refers to an edge carbon atom (a free site), $C(O_2)$ refers to an adsorbed oxygen molecule before formation of the complex takes place, and $(CO)_c$ refers to the stable oxide complex. The effect of the complex on the ratio CO/CO_2 may be interpreted to indicate that more than one type of site is important in the reactions leading to these products. Extensions to this simple mechanism will be discussed.

Reference

1. H. Marsh, Chem. Soc. Spec. Pub. No. 32, p. 13, London (1978).