Oxidation of Graphite by Carbon Dioxide - Carbon Monoxide Gas Mixtures

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Graphite has been considered to be oxidized by carbon dioxide by the following mechanism[1];

$$C + CO_2 \underset{i_2}{\overset{i_1}{\rightleftarrows}} C(O) + CO \quad (1)$$

$$C(O) \xrightarrow[i_3]{} CO \quad (2)$$

where i_1, i_2, and i_3 are rate constants and C(O) is the surface oxide.

From Eqs. (1) and (2) the over-all oxidation rate is expressed as follows;

$$R = i_1P_{CO_2}/(1 + (i_2/i_3)P_{CO} + (i_1/i_3)P_{CO_2}) \quad (3)$$

In this study the over-all oxidation rates were measured in the carbon dioxide - carbon monoxide gas mixtures and the values of rate constants, i_1, i_2 and i_3 for elementary reactions were determined at temperatures from 1100°C to 1175°C. Activation energies for elementary reactions were determined and discussed in connection with the surface oxide.

Experimental

Two types of high purity artificial graphite made from petroleum coke were used. In the course of preparation, graphites A and B were heat-treated at 2400°C and 3000°C, respectively. Both kinds of graphite did not contain any metallic impurities more than 1 ppm, as determined by the spectroscopic analysis.

Results and Discussion

Equation (3) is rewritten in the form;

$$1/R = (1/i_3) + (i_2/i_1 \cdot i_3)(P_{CO}/P_{CO_2}) + (1/i_1)(1/P_{CO_2}) \quad (4)$$

Equation (4) shows that: (1) If the rates are measured at various total pressures with a constant ratio of (P_{CO}/P_{CO_2}), the plot of $1/R$ *vs.* $1/P_{CO_2}$ gives the value of $1/i_1$. (2) The intercept on the axis of $1/R$ (of the above straight line) gives the value of $1/R^\circ = (1/i_3) + (i_2/i_1 \cdot i_3)(P_{CO}/P_{CO_2})$. Moreover, the plot of $1/R^\circ$ *vs.* P_{CO}/P_{CO_2} gives a straight line and the slope gives the value of $(i_2/i_1 \cdot i_3)$ and the intercept on the axis of $1/R^\circ$ gives the value of $1/i_3$. The value of the above slope should coincide with the value of a slope when $1/R$ is plotted against

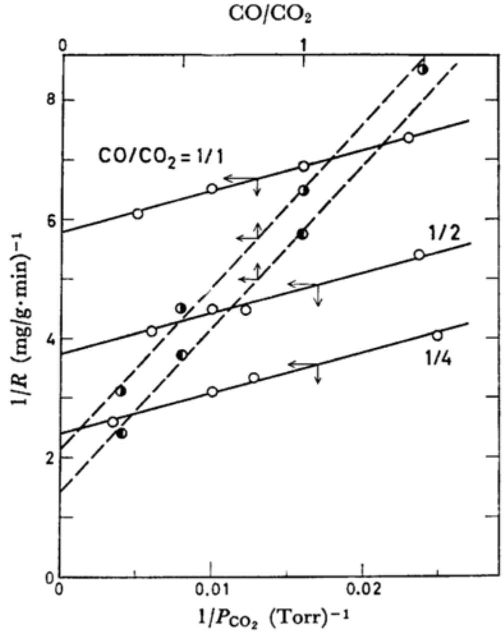

Fig. 1. Plot of $1/R$ *vs.* $1/P_{CO_2}$ and $1/R$ *vs.* P_{CO}/P_{CO_2} of graphite A at 1150°C.
-○-: plots of $1/R$ *vs.* $1/P_{CO_2}$ at constant ratios of P_{CO}/P_{CO_2}
-◑-: plot of $1/R^\circ$ *vs.* P_{CO}/P_{CO_2}
-◐-: plot of $1/R$ *vs.* P_{CO}/P_{CO_2} (P_{CO_2} = 100 Torr)

P_{CO}/P_{CO_2} at a constant partial pressure of carbon dioxide.

The plots of $1/R$ *vs.* $1/P_{CO_2}$ and $1/R$ *vs.* (P_{CO}/P_{CO_2}) are shown in Fig. 1. The values of i_1, i_2 and i_3 are calculated from the values of $1/i_1$, $1/i_3$ and $i_2/i_1 \cdot i_3$. They are shown in Figs. 2 and 3 as Arrhenius plots. The values of activation energies are also given in these figures.

The value of $\Delta H_1 = E_1 - E_2$ gives the enthalpy change of the reaction (1). The values of ΔH_1 obtained in this study are 24 kcal/mol and 20 kcal/mol for graphites A and B, respectively.

Assuming the value of ΔH_1 to be 25 kcal/mol, the enthalpy of formation of surface oxides is calculated as follows.

$$\Delta H^\circ_{f,C(O)} = \Delta H_1 - \Delta H^\circ_{f,CO} + \Delta H^\circ_{f,C} + \Delta H^\circ_{f,CO_2} = 42 \text{ kcal/mol}$$

Bull and co-workers[2] reported the value of the

1) P. L. Walker, Jr., F. Rusinko, Jr. and L. G. Austin, Advances in Catalysis, Vol. 11, Academic Press, New York (1959), p. 133.

2) H. I. Bull, M. H. Hall and W. E. Garner, *J. Chem. Soc.*, **19**, 837 (1931).

heat of adsorption of oxygen on the surface of carbons to be 100 kcal/mol. If the adsorption results in the formation of surface oxide, the heat of formation of this surface oxide is 50 kcal/mol. $\Delta H^\circ_{f,C(O)}$ determinedk inetically in this study seems to meet this value.

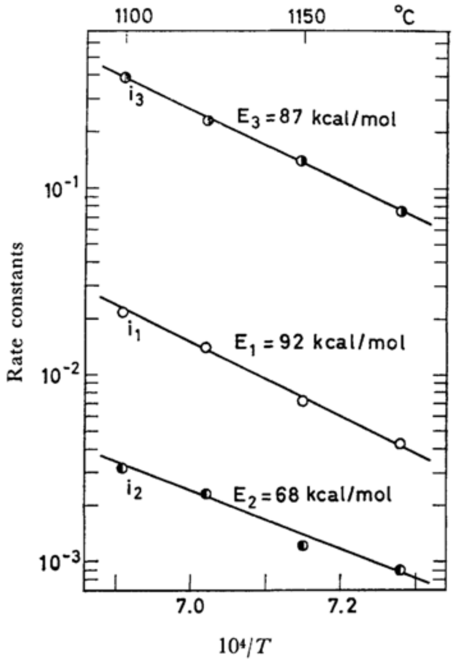

Fig. 2. Arrhenius plots of the rate constants of graphite A.

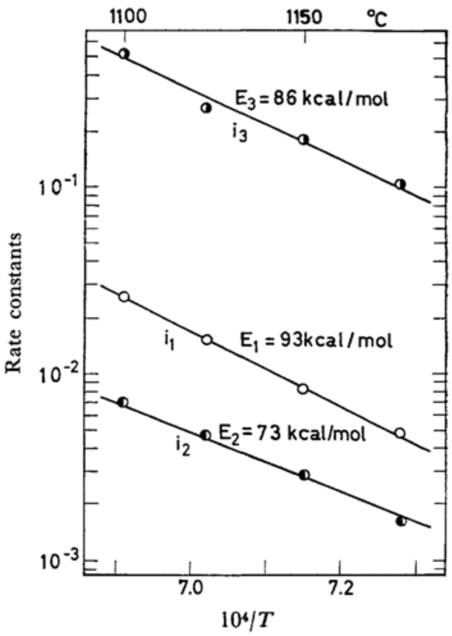

Fig. 3. Arrhenius plots of the rate constants of graphite B.