

APPLICATION OF COMPUTER MODELING TECHNIQUES TO THE KINETICS OF
THE REACTION OF CARBON WITH OXYGEN

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ABSTRACT

Computer modeling techniques are applied to the kinetics of the reaction of carbon with oxygen. The rates of disappearance of oxygen, of formation of CO, CO₂ and the surface complex, measured over the temperature range 748-1173 K and the pressure range 0.5-400 Pa may be described by a mechanism involving adsorption of oxygen, formation of the strongly-bound complex, desorption of the complex and reaction of the complex with a gas-phase molecule of oxygen. The latter is shown to be an important source of CO₂ at low temperatures and higher pressures of oxygen. An important feature of the mechanism is the existence of at least two distinct types of active sites for the binding of the complex on the carbon surface, each with a characteristic reactivity. Most of the results on which the model is based were obtained using thin films of pyrolytic carbon, but some results from the oxidation of graphon are also consistent with the mechanism.

INTRODUCTION

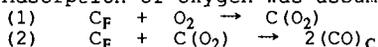
The purpose of the present study is to illustrate the application of computer modeling techniques to the reaction of carbon with oxygen. The kinetics of this reaction have been studied over a period of several decades (1,2) with most emphasis placed on steady-state solutions leading to an interpretation of the order and activation energy of the over-all rate. The importance of the strongly-bound surface complex in the oxidation process was first recognized by Walker and colleagues (3). The properties of the complex have been extensively studied (4,5,6) but its role in the various elementary surface processes involved in oxidation is not understood in detail.

The development of computer modeling techniques has opened the way for the testing and evaluation of mechanisms with far more sensitivity than is possible with steady-state methods. A major requirement in the use of these techniques is the availability of reliable measurements for the rates of the elementary processes in the mechanism. Recently, kinetic studies of the reaction of oxygen with carbon in a static system (7), involving a complete analysis of the time course of the reaction in terms of the depletion of oxygen and carbon and of the formation of carbon monoxide and carbon dioxide, led to an estimate of the concentration of adsorbed species on the surface and of the values

of some of the rate constants for the elementary processes in the reaction. Using these results a mechanism for the reaction has been developed and tested using computer modeling techniques. The present paper reviews the development of the mechanism from the results of the reaction in the temperature range 748 - 898 K and pressures of oxygen of 90 - 133 Pa, where the product was almost entirely carbon dioxide (8), and then describes the extension of the mechanism to results obtained at temperatures up to 1073 K, where carbon monoxide was a major product. Finally, the model was applied to results obtained by Laine, Vastola and Walker, (LVW), (3) at 898 K and at pressures of 0.1 Pa.

EVALUATION OF THE ELEMENTARY PROCESSES IN THE OXIDATION

Details of this interpretation have been described previously (8) and will be reviewed only briefly. The number of active sites, C_F , on the carbon surface used in the experiments, was obtained by measurement of the active surface area, as defined by LVW (3). Adsorption of oxygen was assumed to occur in two steps

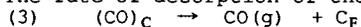


where C_F is a free carbon site and $C(O_2)$ refers to an adsorbed molecule before formation of the strongly-bound complex, $(CO)_C$, takes place. An estimate of k_1 was obtained from the initial rapid decrease in pressure of oxygen observed in experiments below about 848 K, and was calculated from the expression,

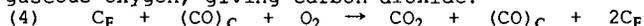
$$-d[O_2]/dt = k_1 C_F^0 [O_2]^0$$

The activation energy for k_1 was about 40 kJ mol⁻¹. It was assumed that k_2 was substantially less than k_1 and the ratio k_2/k_1 was set at 0.1 in the low temperature region.

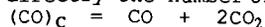
The rate of desorption of the complex



was estimated from the results of temperature-programmed desorption measurements. Because the rate was slow compared to the measured rate of the reaction below about 900 K, a new type of reaction was proposed (7) involving reaction of the complex with gaseous oxygen, giving carbon dioxide.



Estimation of the rate constant for reaction (4) required values for the concentration of each complex on the surface, $C(O_2)$ and $(CO)_C$, as well as the concentration of free sites, C_F , at anytime. The concentration of the strongly-bound complex, $(CO)_C$, was obtained, at any stage of the reaction, by removing reactants, products and $C(O_2)$ by evacuation, leaving only $(CO)_C$ on the surface. Temperature-programmed desorption to 1223 K, with measurement of the carbon monoxide and carbon dioxide evolved, gave directly the number of moles of $(CO)_C$.



Since CO was not a product of the reaction at these temperatures the difference between the measured pressure at any time and the

initial pressure was related to the concentration of both $C(O_2)$ and $(CO)_C$ as follows,

$$P_i - P_0 = -\Delta O_2 = 2(CO)_C + C(O_2)$$

allowing an estimate of the quantity of $C(O_2)$. The concentration of free sites at any time, C_F , was given as the difference between

the initial value, C_F^0 , and the sum of sites occupied by $C(O_2)$ and $(CO)_C$.

$$C_F = C_F^0 - [(CO)_C + C(O_2)]$$

The rate constant for reaction (4) was estimated from the following expression for the rate of disappearance of oxygen, after the initial stage of the reaction.

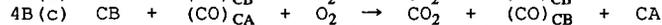
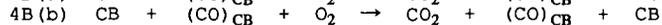
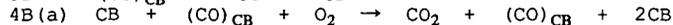
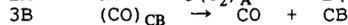
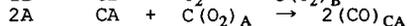
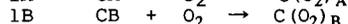
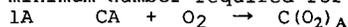
$$-d[O_2]/dt = k_1 C_F [O_2] + k_4 C_F [(CO)_C] [O_2]$$

The values of the rate constants and their Arrhenius parameters are given in Table 1. The concentration of all reactants were expressed as total mol in the particular reaction system, since this allows a direct relation between gas phase and adsorbed molecules, although the values are not transferable to other systems. The calculations used a computer program which has been employed in previous studies (9). It uses the popular DIFSUB integrator and has provision for first order sensitivity analysis and automatic adjustment of kinetic parameters to fit experimental yield-time data.

DEVELOPMENT OF THE MODEL

A. TEMPERATURES BELOW 898 K

The reactions described formed the starting point for the development of the mechanism, but, as expected, were not sufficient to describe the yields of products and consumption of reactants over the complete course of the reaction. Only by introducing two types of active sites, C_A and C_B , with different reactivities and a certain amount of interconversion, was agreement obtained between the calculated and observed results. Because of the different reactivities not all the reactions were important for each type of site. The following set, which includes several variations of reaction (4), represents the minimum number required for quantitative agreement.



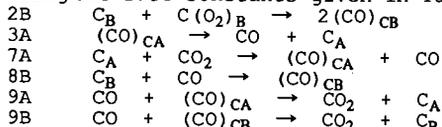
The mechanism was tested at temperatures of 748, 798, 848 and 898 K and an example of the results is shown in Figure 1a. In the figures the points represent the experimental measurements and the lines represent the calculated values. The rate constants giving the best fit at each temperature were further adjusted to conform

to an Arrhenius temperature dependence and the final values are those given in Table 1.

From this mechanism the following picture of the reaction emerges. The sites designated C_A adsorb oxygen rapidly and are quickly saturated, while the sites C_B adsorb oxygen more slowly and participate in other reactions. The very different nature of adsorption on C_B sites is reflected in the larger activation energy for reaction 1B compared to 1A. Reactions which are kinetically described by reaction (4), with the variations listed as (a), (b) and (c), can account for the formation of carbon dioxide, but at these temperatures appear to occur mainly on B sites. Nevertheless interconversion of the sites through reaction (5) was important. Reaction (3) is included here but makes little contribution at these temperatures. It should be noted that several other types of surface processes involving both $C(O)_C$ and $C(O_2)$ were initially included in the mechanism, but, using reasonable values for rate constants, were not found to contribute significantly.

B. TEMPERATURES ABOVE 898 K

While the simple mechanism, with rate constants conforming to an Arrhenius dependence, gave reasonable agreement with the measurements up to 898 K, it became clear that further reactions were needed to describe the reaction at higher temperatures. One desorption reaction was no longer adequate and desorption of carbon monoxide from A sites was included, using a higher activation energy and frequency factor than for desorption from B sites. Above about 1000 K adsorption on and reaction with the carbon surface became important for both products, carbon monoxide and carbon dioxide. Also at these temperatures the A sites began to dominate the reaction. The following reactions were added, using the rate constants given in Table 1.

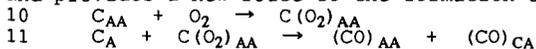


An example of the calculated and measured yields of products and consumption of reactants is shown in Figure 1b.

C. COMPARISON OF THE MODEL WITH THE RESULTS OF LVW

The model presented provided a reasonably quantitative description of the results obtained from a study of the reaction of oxygen with pyrolytic carbon in the form of a thin film on the surface of a quartz reactor. To test the generality of the mechanism the model was applied to the results of LVW obtained from a study of the reaction with Graphon at 898 K and pressures of oxygen of ~0.1 Pa. By introducing two alterations to the mechanism good agreement was obtained between predicted and observed results. First, the rate constants in reactions 2A and 3A were increased by factors of

14 and 120 respectively, reflecting the high reactivity of Graphon. Secondly, a new type of adsorption site, designated C_{AA} , was introduced, which rapidly but loosely binds oxygen, reaction (10), and provides a new route to the formation of $(CO)_{CA}$, reaction (11).



The rate of reaction (10) is the key factor in reproducing the decay curves of oxygen observed by LVW (3). The new type of site binds a single oxygen atom particularly strongly, and may give the very stable complex suggested by LVW. The results calculated from the revised mechanism are compared with the results of LVW in Figure 2a and in Figure 2b the previous mechanism (without reaction (10) and (11)) is compared with the results of ref (7) at the same temperature.

DISCUSSION

The most significant features of the model are the existence of at least two distinct types of active sites on the carbon surface, with different reactivities, and the introduction of the general type of reaction given by equation (4), where a gas-phase molecule of oxygen reacts with the chemi-sorbed complex. Although rate constants for these reactions were based on measurements made in a particular system with a particular type of carbon, the basic features of the mechanism should be generally applicable to the reaction of oxygen with carbon.

The idea that the carbon surface may contain more than one type of active site has been suggested many times, based on results from a variety of studies. The model clearly shows the difference in reactivities of the A and B sites, not only in the rate constants for reactions 1 and 2 but in reaction 3 and the subsequent reactions. The relative values for these rate constants as well as the relative concentrations of the sites may change with different types of carbon and indeed the modifications to the mechanism to provide agreement with the results of Laine, Vastola and Walker were essentially of this sort.

Reaction (4) and its variations account for the fact that carbon dioxide is a primary product of the reaction and that its rate remains dependent on the pressure of oxygen even at high pressure. Furthermore these reactions will undoubtedly have activation energies lower than that of direct desorption and will be important at temperatures where the latter is still slow.

The model also shows that the role of the complex resembles that of active sites in a catalytic process. The complex is a reaction intermediate, even though new carbon atoms are continuously involved in its formation, and, as suggested previously (7), the rate may be expressed as a turn-over number, based on the concentration of complex on the surface. Rates from a variety of studies, for which the number of active sites had been measured, were in reasonable agreement when expressed in this way.

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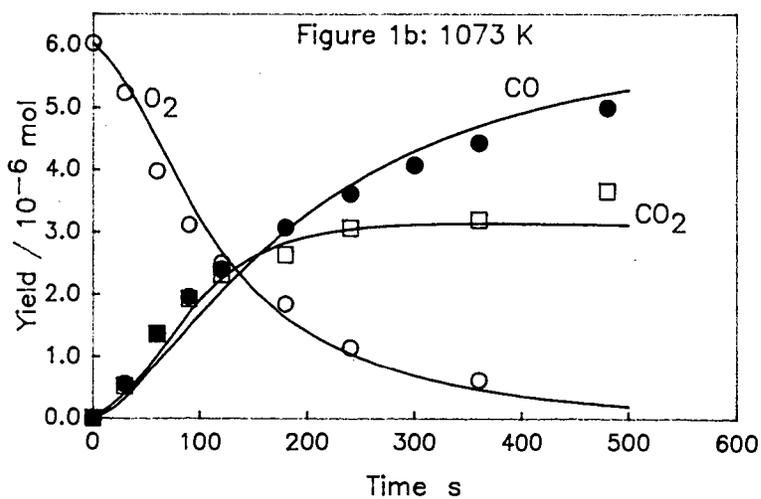
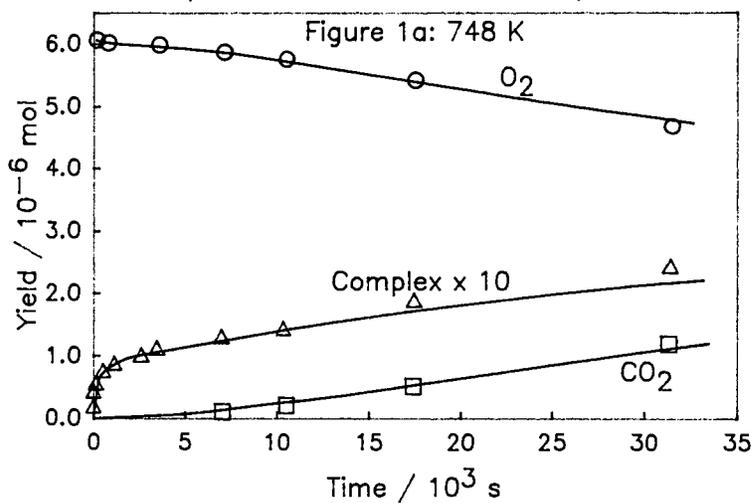
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TABLE 1

Rate constants used in obtaining the results in Figures 1 and 2.

Reaction	k ₇₄₈	k ₈₉₈	k ₁₀₇₃	unit
1A	3.51×10^2	1.35×10^3	4.01×10^3	$\text{mol}^{-1}\text{s}^{-1}$
2A	7.45×10^2	1.43×10^4	1.58×10^5	$\text{mol}^{-1}\text{s}^{-1}$
3A	0	3.76×10^{-4}	3.51×10^2	s^{-1}
5A	2.61×10^2	2.51×10^4	1.03×10^6	$\text{mol}^{-1}\text{s}^{-1}$
7A	0	0	8.83×10^5	$\text{mol}^{-1}\text{s}^{-1}$
9A	0	0	1.50×10^9	$\text{mol}^{-1}\text{s}^{-1}$
1B	0.105	17.3	1.10×10^3	$\text{mol}^{-1}\text{s}^{-1}$
2B	0	0	1.00×10^5	$\text{mol}^{-1}\text{s}^{-1}$
3B	0	0	5.04×10^{-2}	s^{-1}
4B (a)	2.14×10^8	1.20×10^{10}	3.18×10^{11}	$\text{mol}^{-2}\text{s}^{-1}$
4B (b)	7.17×10^5	1.01×10^9	3.69×10^{11}	$\text{mol}^{-2}\text{s}^{-1}$
4B (c)	1.61×10^8	3.90×10^8	8.02×10^8	$\text{mol}^{-2}\text{s}^{-1}$
8B	0	0	6.00×10^2	$\text{mol}^{-1}\text{s}^{-1}$
9B	0	0	1.28×10^6	$\text{mol}^{-1}\text{s}^{-1}$

Comparison of Model and Experiment



Comparison of Model and Experiment at 898 K

