

# THERMAL DESORPTION ANALYSIS OF OXYGEN SURFACE COMPLEXES ON CARBON

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**Abstract**—The energetics of oxygen surface complex groups bound to a carbon surface were investigated using linear-temperature programmed thermal desorption. The rate of CO production from the decomposition of surface complex formed by the low temperature oxygen chemisorption on an activated Graphon surface indicated that at least two types of functional groups and/or sites must exist. In addition the data indicate that the desorption energies of these groups and/or sites is a function of their coverage. Mathematical modeling has also shown that those workers using the step-temperature programmed thermal desorption technique would not have energy resolution sufficient to detect surface heterogeneity.

## 1. INTRODUCTION

Surface energy characteristics of graphitic materials are of great interest. Graphites with different surface natures have different combustion rates[1, 2], act differently in various prosthetic devices[3, 4], exhibit unique electrical[5, 6] and catalytic properties, and have varying wettabilities and adsorptive qualities[7, 8].

The graphite structure has both a  $\pi$ -bonded[9], rather inert, planar surface, and very reactive (having unpaired  $sp^2$  electrons[10]) "zig-zag" and "arm-chair" edge surfaces. Chemisorbed oxygen on the reactive surfaces can be in the form of various functional groups[8, 11-14] that are important in influencing further surface reaction. Hennig[2] and Thomas[15] found that the two edge surfaces have different oxidation speeds. Thus, a functional group bound to a "zig-zag" surface would be energetically different than the same functional group bound to an "arm-chair" surface. Also, since most industrial graphites are turbostratic[16], the layers are not ordered in the  $c$ -direction, groups bound between layers can have different bond lengths giving rise to different bonding energies[17].

Therefore, the study of chemisorbed species on carbon surfaces involves at least two energetic variables: functional groups and reactive surfaces. These two variables could produce even further variances. That is, there may be interactions between the functional groups as their population increases on the surface, or possibly the additional bonding might affect the electro-negativity (Fermi Level) of the carbon surface since the  $\pi$ -electrons are mobile. Because of these possibilities and the practical importance of oxygen groups, a study of the rate of thermal desorption of such complexes bound to a sample of Graphon, a highly characterized[5, 18-23] graphitic material, was made. Graphon is graphitized Spheron-6, a turbostratic carbon black, also well characterized[16, 24-27].

During the process of thermal desorption the oxygen remains bonded to carbon atoms and comes off the surface as CO and CO<sub>2</sub>, both as primary products[5, 28, 29]. The kinetic nature of the complexes (functional groups and/or sites) that produce CO can be

inferred by trapping out any CO<sub>2</sub> formed (usually less than 5-10% of the total gases), and monitoring the CO pressure increase in a closed volume as a function of time.

Table I[8, 11-14] contains those functional groups that might form as a result of oxygen chemisorption on graphite.

In summary, a difference between two kinetic species could arise either from the decomposition of the *same* functional group bound to two structurally different types of sites or from the decomposition of *different* functional groups themselves.

The breaking of functional groups is a unimolecular fission process[30, 31]. If S-CO is the surface bound carbon monoxide, the rate equation with an Arrhenius constant[32] for the process is

$$\frac{d(\text{CO})}{dt} = A(\text{S-CO})^n \exp(-E_d/RT) \quad (1)$$

where  $d(\text{CO})dt^{-1}$  is the rate of change in concentration of CO (in this case the rate of appearance of CO),  $A$  the frequency factor (a measure of the number of effective collisions or vibrations that the molecules undergo),  $n$  the reaction order (equals one for decompositions not requiring collision processes or additional reactants),  $E_d$  the activation energy for desorption,  $R$  the universal gas constant and  $T$  the absolute temperature.

Table I. Functional groups on carbon

Functional groups	Decomposition products
carbonyl	CO
quinone	CO
ether†	CO
carboxylic anhydride	CO, CO <sub>2</sub>
lactone	CO <sub>2</sub>
lactol†	CO <sub>2</sub> , H <sub>2</sub> O
carboxylic acid	CO <sub>2</sub> , H <sub>2</sub> O
phenol (hydroxyl)	CO, H <sub>2</sub> O
hydroquinone	CO, H <sub>2</sub> O
aldehyde	CO, H <sub>2</sub> O

†Probably rather scarce.

A homogeneous surface with non-interacting groups has a constant frequency factor and desorption energy[33]. Consequently, if a temperature is chosen that gives a measurable rate of desorption, the total desorption will occur within a reasonable time. For Graphon, and other graphitic materials, the complexes initially decompose quite rapidly at temperatures anywhere above 600°K[12]. However, in the temperature range from 600 to 1250°K the reaction rate quickly become much slower[34] than predicted by eqn (1) after only a fraction of the complexes has decomposed. To realize further decomposition the temperature must again be raised. Complete decomposition in a reasonable length of time (12 hr) is only achieved at the maximum temperature of about 1250°K[35]. This behavior suggests that there are multiple functional group and/or site combinations with different rates of desorption or that there is a single functional group and/or site combination whose rate of decomposition is a function (linear, Gaussian, Poissonian, etc.) of coverage. Such cases would require that after a fraction of the complex has decomposed, the remainder must have lower frequency factors and/or higher activation energies of desorption so that a further temperature increase is required for additional desorption. This experimental finding is in line with the earlier discussion about the varying surface reactivities and possible population effects of graphite.

Essentially two techniques[31, 36–40] have been used by investigators studying the desorption of oxygen groups from graphites: that of monitoring the desorption while programming the temperature over a series of isothermal steps of ascending temperature [step-temperature programmed desorption (step-TPD)] and that of monitoring the desorption products while linearly increasing the desorption temperature [linear-temperature programmed desorption (linear-TPD)]. Interestingly, the interpretations of the process have largely depended upon the technique used.

Tucker and Mulchay[41], Dollimore *et al.*[42], Weber[34] and Barton *et al.*[43], have used step-TPD. Their results are summarized in Table 2. These researchers indicate that there is one type of kinetic species where the energy of desorption,  $E_d$ , is a continuous function of surface oxide coverage. Both linear and Gaussian distribution functions have been found. All of these investigators found an Elovich type behavior. That is, for each increase of temperature the rate of decomposition increases and then rapidly decreases.

Phillips *et al.*[44] and Bansal *et al.*[45] used the linear-TPD technique in a static system and measured the resultant pressure of the desorbed species. Phillips found that it was not possible to draw a smooth curve through the desorption data points and concluded that desorption of several discrete kinetic species was taking place. Bansal was able to depict linear regions in the desorption pressure vs time curve. By plotting the slope of that curve he found evidence of four types of kinetic species.

Feates and Keep[46] used linear-TPD in a flow system and measured the partial pressure of the decomposition products. This method directly measures the rate of decomposition. For the case of CO evolution from a

Table 2. Results using STEP-TPD

Refs.	Sites	$E_d$ distribution function	$E_d$ range (kJ mol <sup>-1</sup> )
[41]	1	linear	256–451
[42]	1	Gaussian	167–544
[34]	1	linear	0–600
[43]	1	Gaussian	90–500

thermally generated oxygen complex, they observed three distinct maxima in the rate of decomposition, indicating at least three types of kinetic species. For the three kinetic species they calculated  $E_d$ 's of 262, 275 and 283 kJ mol<sup>-1</sup>. Feates and Keep concluded that although the desorption process took place for a multiplicity of kinetic species spanning wide ranges of energy, desorption actually takes place by surface migration to specific active sites of well defined  $E_d$ .

LeBail[47] also used linear-TPD in a flow system. In order to fit the desorption rate vs time curve it was necessary to postulate a spectrum of activation energies. The best fits were obtained by using a number of discrete kinetic species, each having a Poisson distribution of energies separated by equal increments of energy. Magne and Duval[48] found that the CO desorption rate spectrum produced by the linear-TPD flow technique had four separable peaks indicating four kinetic species.

Therefore, we see that the step-TPD technique leads to a one kinetic species hypothesis and the linear-TPD technique leads to a multiple kinetic species hypothesis. This discrepancy is most likely because the energy differences due to the breakage of different functional groups and/or different surfaces, and also the spans of the energy distribution functions due to population and/or surface variation effects are not large (0–50 kJ mol<sup>-1</sup> is an estimate). Desorption involves carbon-carbon bond breakage. The energy necessary for breakage of this bond is about 336 kJ mol<sup>-1</sup> in most organic reactions[49]. Although it is the premise of these investigations that there are differences either in the way the oxygen is bonded to the surface or in the surfaces themselves, still it is to be understood that the desorption curve is always due to carbon-carbon bond breakage. So there will be subtle variances at best. It is unlikely that those investigators using step-TPD with its relatively large temperature increments would have the resolution to detect these energy differences. If there are multiple kinetic species and/or distributions influencing bonding energies, then linear-TPD with its capability of continuously monitoring the rate of desorption would have the best chance of detecting their presence. Since linear-TPD promises to give the most analytical insight of the desorption phenomenon it will be discussed in further detail.

Considering first the rate eqn (1), if the rate of change of temperature,  $T$ , is linear with time,  $t$ , then  $T = T_0 + bt$ . On differentiation  $dT dt^{-1}$  equals  $b$ , the heating rate. The overall rate equation then becomes[38–40].

$$\frac{d(\text{CO})}{dT} = \frac{A}{b} (\text{S-CO}) \exp(-E_d/RT) \quad (2)$$

Computerized mathematical modeling using eqn(2), or its integrated form, becomes relatively simple since time is removed as a variable. Such modeling gives insight into how well one can discern various kinetic entities and identify their energy distributions. Considering the previous discussion of functional groups, graphitic surfaces, and appropriate rate equations, the following possible surface complex decomposition models need to be considered:

- (1) a discrete kinetic species on a homogeneous surface
- (2) more than one discrete kinetic species; that is, step heterogeneity
- (3) a continuously changing kinetic species; that is continuous heterogeneity
- (4) more than one continuously changing kinetic species; that is, step plus continuous heterogeneity.

Each of these models can be evaluated by setting the parameters for rate equations such that the temperature of maximum decomposition coincides with that of the experimental data. Then the calculated desorption curve can be contrasted with the experimental data. However, caution must be exercised because any given complicated curve can be resolved into a number of given components, some that may be just mathematical constructs. The fitting of desorption rate curves by summing various kinetic equations with varying parameters is more reliable the simpler the model. In addition, the ruling out of a possibility is more likely correct than its identification. For example, if an equation cannot be made to fit the experimental data by varying its parameters, then there is little chance that the physical condition modeled by the equation exists. However, if summed equations could be made to fit the experimental data, possibly a lesser or greater number of summed equations could be made to fit, the researcher not knowing which one of these situations is correct physically. Therefore, modeling is more definitive in its possibility for exclusion than inclusion.

## 2. EXPERIMENTAL

The carbon used was Graphon, a graphitized carbon black supplied by the Cabot Corporation. The sample was burned-off to 16% weight loss by reacting with air for 120 hr at 800°K. The BET surface area was 90 m<sup>2</sup> g<sup>-1</sup> and the active surface area as determined by the method of Laine[50] was 2.3 m<sup>2</sup> g<sup>-1</sup>. A 0.147 g sample was placed in a static reactor system with a volume of 20l and cleaned by heating to 1300°K for 48 hr in a vacuum of 10<sup>-5</sup> Pa. The apparatus is described in more detail elsewhere[51].

This paper reports on the measurement of the rate of CO production using a linear-TPD of 3°K min<sup>-1</sup> going from about 300 to 1300°K to decompose surface complexes. The complexes were formed by chemisorbing dry oxygen at room temperature and atmospheric pressure for 2 hr on the thoroughly cleaned Graphon surface. Of the functional groups from Table 1 that could form, one can omit lactol, carboxylic acid, phenol [hydroxyl], hydroquinone and aldehyde if there is a thorough removal of hydrogen from Graphon's surface. Carboxylic

anhydride can be omitted if the chemisorptions are done below about 575°K according to Weber[34]. Therefore, under these conditions carbonyl, quinone, ether and lactone are probably contributors to the CO and CO<sub>2</sub> that are produced on desorption.

The CO produced was allowed to accumulate in the reactor while the CO<sub>2</sub> was condensed in a liquid nitrogen trap. The final pressure of CO in the system was approximately 0.75 Pa. The pressure was measured by using a modified Baratron electronic differential manometer. The sensitivity of the manometer was 0.1 mPa. A PDP-9 digital computer was used to control the heating rate and record temperature and pressure. During a typical 5.5 hr run approximately 1600 readings would be taken. Data were recorded on magnetic tape for further processing.

## 3. RESULTS AND DISCUSSION

Data obtained for each run consist of CO pressures recorded vs time. The one point of total agreement in all of the thermally induced surface complex decomposition studies is that the one kinetic species, discrete  $E_d$ , model is inoperative. This fact can be seen in Fig. 1 which contrasts numerical solutions of single kinetic species models with the experimental data, curve A, obtained in this investigation. With an activation energy of 126 kJ mol<sup>-1</sup>, the integrated desorption curve B is almost a step function. The activation energy has to be set at the unrealistically low value of 50 kJ mol<sup>-1</sup>, curve C, in order to have the simulated curve approximate the experimental data.

Although Feates and Keep[46] suggest a model with three kinetic species, each with a discrete  $E_d$ , such a model is difficult to rationalize in view of the results obtained by workers using the step-TPD technique[34, 41-43]. They found that at each isothermal step the decomposition would follow Elovich kinetics, which usually signifies a variable  $E_d$ . If  $E_d$  were single valued for a given kinetic species at any temperature

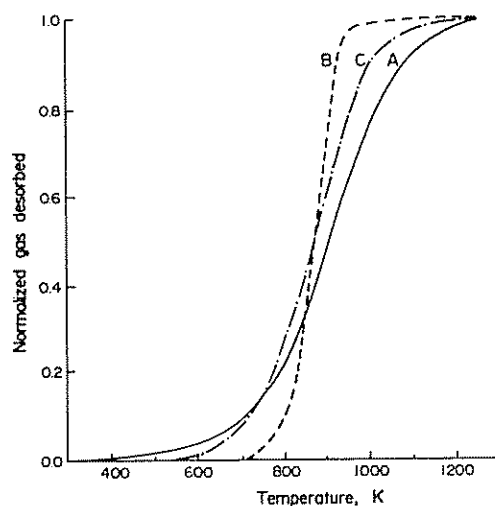


Fig. 1. Integrated linear-TPD desorption curves for (A) the experimental data, (B) a model with an  $E_d$  of 126 kJ mol<sup>-1</sup> and (C) a model with an  $E_d$  of 50 kJ mol<sup>-1</sup>. Total amount of CO desorbed was 0.95 cc g<sup>-1</sup> (STP)

where desorption of that kinetic species was measurable most of the functional groups bound to the site should be able to be removed. Although the investigators using step-TPD found different distribution functions of  $E_d$ , Table 2, they all agree that the distribution function was continuous. This is in sharp contrast to the researchers using linear-TPD, who found evidence for more than one kinetic species.

On observation, the CO pressure vs time curve of the experimental data in Fig. 1 appears to be continuous; however, the eye is not capable of detecting subtle changes in an integrated function. The resolution of multiple functional groups and/or sites obtainable with linear-TPD is dependent upon the heating rate, the relative amount of each kinetic species, and the spread of the activation energy of desorption. The differential (rate) curve is more sensitive to variations that would differentiate between model (3), a single continuously changing kinetic species, and model (4), more than one continuously changing species.

The experimental curve used in this investigation is made up of 1600 data points per run, a running differential,  $\Delta P \Delta T^{-1}$ , of each of the nine identical runs was generated with a  $\Delta T$  of 18°K. These differentials were smoothed twice, averaging every five adjacent points, weighted equally, into the center one, and then summed. This composite is shown in Fig. 2, Curve A. To look for deviations, each individual curve was compared with the composite. The same basic character was shown for all curves: the same approach and decline from the maximum rate and especially the same double peak character on the high temperature side of the differential maximum.

In mathematical modeling of linear-TPD rate curves, one anomaly is of great interest: an inflection point. If one occurs it means that at least two separate kinetic species (functional groups and/or sites) exist. Otherwise there would have to be an inflection in the energy function itself, meaning that species with lower energies

would come off later than ones with higher energies, which is not possible.

Extensive mathematical modeling has shown that this rate curve cannot be reproduced by a single kinetic species mechanism with a simple  $E_d$  distribution function. Specifically, no single kinetic species mechanism can account for the gradual approach to and decline from the point of maximum rate of desorption. To model the experimental curve using multiple kinetic species with discrete  $E_d$ 's would require postulation of a large number of separate sites. Curve B in Fig. 2 is an example of a single kinetic species with a single  $E_d$  (50 kJ mol<sup>-1</sup>). The number of discrete kinetic species necessary to model the desorption curve is greatly reduced when the  $E_d$  for each kinetic species is allowed to vary with coverage for that particular site. Curve C in Fig. 2 is an example of a single kinetic species mechanism with an  $E_d$  that varies linearly with coverage from 110–140 kJ mol<sup>-1</sup>. These factors tend to indicate that the complexes formed on graphite consist of several types of functional groups located on several types of active sites and that the desorption of each of these complexes is a function of the coverage.

It is possible to calculate the energy function vs coverage, assuming the pre-exponential factor, A, to be derived from the transition state theory[32] with the entropy part equal to 1.0[32, 52, 53], that is no configurational changes during desorption, and the vibratory part equal to  $kTh^{-1}$ [30],  $T$  going from 300 to 1300°K and  $kTh^{-1}$ , therefore, going from 8 to 30 THz. Having the relationship of the energy function vs coverage, it is then possible to plot the amount of chemisorbed surface having a particular desorption energy vs the desorption energy itself. If one does so with the experimental data two maxima at 270 and 295 kJ mol<sup>-1</sup> occur (Fig. 3). A value of about 300 kJ mol<sup>-1</sup> might be expected since the carbon-carbon single bond strength in an electronically neutral environment is about 336 kJ mol<sup>-1</sup> at 300°K[49], and both higher temperatures and the electronegativity of the oxygen groups would cause the bond energy to be lower.

Although the decomposition of carbon-oxygen complexes is an involved process, two points can be made. First, there must be more than one functional group and/or site, and second, the activation energies for the

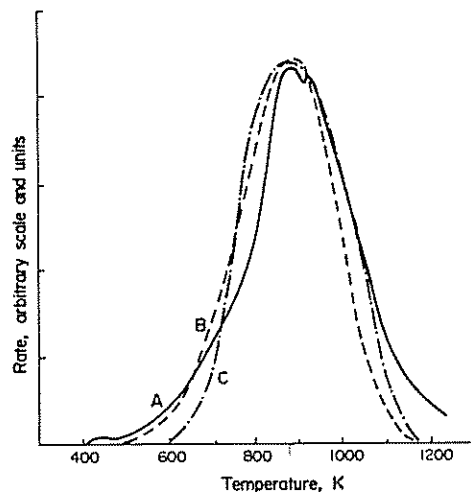


Fig. 2. Differentiated linear-TPD desorption curves for (A) the experimental data, (B) a model with an  $E_d$  of 50 kJ mol<sup>-1</sup> and (C) a model with a linearly varying  $E_d$  from 110 to 140 kJ mol<sup>-1</sup>. Maximum rate of desorption was  $1.7 \times 10^{-2}$  cc g<sup>-1</sup> min<sup>-1</sup>.

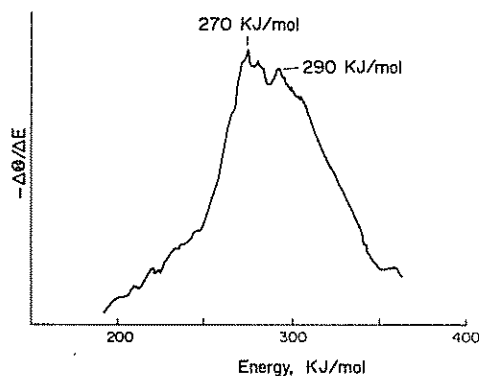


Fig. 3. Energy distribution function of the surface complex.

decomposition of these complexes must be a distributed function. As a consequence, the analysis of the energetics of the thermal desorption of these complexes is best accomplished by linear-TPD.

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