

OXYGEN-18 TRACER STUDIES ON
THE CARBON-OXYGEN REACTION

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Reactions for the production of carbon dioxide when oxygen reacts with carbon are considered. In order to determine which reaction(s) is of primary importance, oxygen-16 and oxygen-18 (in molecular oxygen, carbon monoxide and carbon dioxide) are used. Reactions of the above molecules (always at a total pressure <100 millitorr) with the graphitized carbon black, Graphon, are followed by monitoring continuously reactant and product pressures mass spectrometrically. It is shown that carbon dioxide is a primary product of the carbon-oxygen reaction. The intermediate for carbon dioxide production involves atomic oxygen on the carbon surface, or the reaction can be written $2C + O_2 \rightarrow 2C(O)_i \rightarrow CO_2 + C$. Possible exchange reactions on the carbon surface, which could lead to misinterpretation of the results, are investigated.

I. Introduction

The formation of carbon dioxide in the reaction of carbon and oxygen has been the subject of numerous studies. However, the mechanism of carbon dioxide formation is still not known. There has been disagreement as to whether carbon dioxide is a primary product of carbon oxidation. That is, is it formed by the direct interaction of carbon and oxygen or from a secondary reaction such as the reaction of gaseous carbon monoxide and oxygen? Walker, Rusinko and Austin (1)

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analyzed the literature on this subject and came to the conclusion that carbon dioxide is a primary product, along with carbon monoxide. The recent work of Laine, Vastola and Walker (2) has confirmed these conclusions. Frey (3), using C^{14} -tagged carbon monoxide and carbon dioxide, has also reached the same conclusion. It is now generally accepted that both carbon monoxide and carbon dioxide are formed by the direct interaction of carbon and oxygen.

Wang and Fleischer (4) attempted to determine if carbon dioxide was formed through an atomic or molecular oxygen intermediate. They reacted O^{18} -enriched oxygen with carbon (both activated charcoal and powdered graphite) by heating the carbon in the oxygen atmosphere in a sealed glass tube. The heating was done with a "micro-burner". Upon heating, the carbon "sparked" and the combustion was usually finished in a few seconds. They concluded that, since the O^{18} was randomly distributed in the carbon dioxide produced, the oxygen atoms in the carbon dioxide had come from different oxygen molecules. The implication here is that an intermediate state involving dissociated oxygen molecules was involved. However, this conclusion may not be justified on the basis of Wang and Fleischer's work due to the experimental conditions of their study. The carbon must have been at a very high temperature to spark. At this high temperature it has been shown that carbon monoxide is the main primary product of the reaction. Day (5) found that at $1200^{\circ}C$ the CO/CO_2 ratio was 28; and using Arthur's equation (6) to predict this ratio at $1500^{\circ}C$, one calculates a value of 63. In Wang and Fleischer's experiments, carbon dioxide was the main product, CO/CO_2 of ca 0.3. This may indicate that the majority of the carbon dioxide was produced as a secondary reaction, probably from gaseous oxidation of carbon monoxide as it leaves the hot carbon surface. This secondary reaction would also give a random distribution of O^{18} in the carbon dioxide product.

A common schematic way of writing the mechanism of carbon dioxide formation is [see for example (7)]:
 $xC + O_2 \rightleftharpoons C_x(O_2) \rightleftharpoons CO_2 + C_{x-1}$ where $C_x(O_2)$ is an intermediate state involving reversibly-adsorbed oxygen molecules. This is done in spite of the fact that reversibly-adsorbed molecular oxygen on carbon has never been proven experimentally. On the contrary, it has been shown by many workers that above $100^{\circ}C$, where physical adsorption is no longer important, adsorbed oxygen can only be removed from a carbon surface as carbon monoxide or carbon dioxide. The above equation is

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usually postulated to explain the observed oxygen pressure dependence of a kinetic study.

The present work was undertaken with the aim of resolving some of these problems of carbon dioxide formation in the carbon-oxygen reaction.

II. Experimental

A. Materials - The carbon used in this study was Graphon (a granular, graphitized carbon black, Spheron 6), obtained from the Cabot Corporation. The surface area (BET) of the original material was $76 \text{ m}^2/\text{g}$. Graphon samples were preoxidized to 14.4 per cent weight loss at 625°C in 500 millitorr oxygen. This pretreatment increased the BET surface area to $98 \text{ m}^2/\text{g}$ --a fractional increase of ca 1.3. However, the area of the carbon sample which adsorbed oxygen at 300°C increased from 0.3 per cent to 3.0 per cent of the BET area for the 14.4 per cent weight loss sample (2)--an increase of ca 10 fold. The reaction rate was approximately proportional to this latter area rather than the BET area (2). Samples of ca 0.1 g of the preoxidized Graphon were used. Because of the prior burn-off, the active area of the Graphon increased to a negligible extent, as a result of small amounts of additional burn-off during isotopic studies.

The O_2^{16-16} used in the tracer studies was Research Grade, obtained from Air Products and Chemicals Company. The major impurities were nitrogen (46 ppm), argon (407 ppm), and water (1.3 ppm). The oxygen used for sample preoxidation was Extra Dry Grade, obtained from the Matheson Corporation. Its minimum purity was 99.6 per cent; further drying of the oxygen was accomplished with liquid nitrogen traps.

The O_2^{18-18} was obtained from YEDA Research and Development Company Ltd. of the Weizmann Institute of Science, Rehovoth, Israel. Mass spectrometric analysis gave 96.8 mole per cent O_2^{18-18} and 98.6 atom per cent O^{18} . This oxygen was used without further purification.

The carbon dioxide and carbon monoxide used for calibration and in reaction mixtures were obtained from the Matheson Corporation. The carbon dioxide was Bone Dry Grade of 99.8 per cent minimum purity; the carbon monoxide was C. P. Grade, which has a minimum purity of 99.5 per cent.

The CO_2^{18-18} and CO^{18} were prepared by oxidizing Graphon with O_2^{18-18} in the reaction system and separating the carbon monoxide and carbon dioxide using a liquid nitrogen trap.

B. Apparatus - Fig. 1 is a schematic diagram of the

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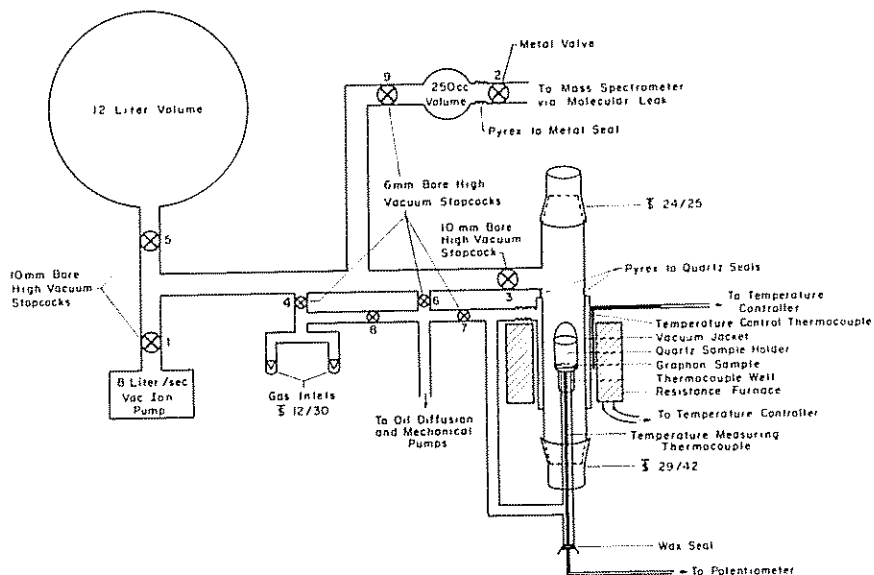


Figure 1. Schematic Diagram of the Reaction Apparatus.

reaction apparatus used in these studies. The apparatus was constructed of Pyrex glass except for the reaction tube, which was double-walled, fused quartz. The annular volume, enclosed by the double wall, was evacuated to prevent significant diffusion into the reaction tube from the atmosphere at the highest temperatures used in this study. The glass vacuum stopcocks were lubricated with Apiezon N grease.

The system was evacuated to 10^{-6} torr with an oil diffusion and mechanical fore pump and then to approximately 10^{-8} torr with an 8-liter/sec Vac Ion pump. The system was connected to a modified General Electric mass spectrometer through a molecular flow leak. The partial pressures of each of the gaseous species could be measured continuously during a reaction. Corrections for the small amount of gas which leaked into the mass spectrometer were made where necessary.

The temperature was controlled to $\pm 0.5^\circ\text{C}$ by a Leeds and Northrup series 60 temperature controller and chromel-alumel thermocouples to control a one kw resistance furnace.

The total volume of the reaction system was 13.02 liters. This large volume was necessary, at the low oxygen pressures used (1 to 50 millitorr), in order to have a reasonable

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amount of reactive gas in the system.

C. Experimental Conditions and Procedure - Before each reaction, the carbon sample was degassed at 950-975°C until a vacuum of approximately 10^{-8} torr was achieved in the system. The temperature was lowered, while pumping on the system, to the desired value. The reaction gas mixture was then introduced to the system through stopcock 4, after closing stopcocks 1 and 3. The pressures of the various gases were measured with the mass spectrometer; then stopcock 3 was opened to start the reaction. The expansion ratio from the volume with stopcock 3 closed to the volume with stopcock 3 open was determined previously, and thus the initial pressures at time equal zero could be calculated. The pressure of each species was measured during the reaction; at the end of the reaction the gas was pumped off to a pressure of ca 10^{-6} torr at the reaction temperature. After closing off the pump, the temperature was raised to 950°C; and the adsorbed oxygen was measured as carbon monoxide and carbon dioxide which desorbed from the carbon surface. In order to clean the surface for the next experiment, the Vac Ion pump was opened and the temperature was increased to 975°C and held at that temperature until a vacuum of 10^{-8} torr was again achieved.

The mass spectrometer was calibrated, using the appropriate pure gases, before and after each reaction. Since the gaseous products to be analyzed were CO, O₂ and CO₂ with both O¹⁶ and O¹⁸ present, the masses of concern were: 28-CO¹⁶, 30-CO¹⁸, 32-O₂¹⁶⁻¹⁶, 34-O₂¹⁶⁻¹⁸, 36-O₂¹⁸⁻¹⁸, 44-CO₂¹⁶⁻¹⁶, 46-CO₂¹⁶⁻¹⁸ and 48-CO₂¹⁸⁻¹⁸.

III. Results and Discussion

When oxygen reacts with carbon, three products have been identified: carbon monoxide, carbon dioxide, and a stable surface oxide, which can only be completely recovered by heating at temperatures considerably higher than reaction temperature (2). This stable surface oxide is mainly recovered as carbon monoxide; thus, it is written as C(O). Previous results have also shown that a reactive intermediate must be present on the carbon surface in small quantities during the gasification of carbon by oxygen (8). Since it has also been shown that carbon monoxide is a primary product of the carbon-oxygen reaction (2,8), this intermediate is written as C(O)_i. Possible reactions for the formation of carbon dioxide when carbon is exposed to oxygen can now be

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listed in Table 1. In reaction (h), $C(O_2)_i$ represents a chemisorbed oxygen molecule as a reaction intermediate.

Before using O^{18} to study these reactions it was first necessary to determine if O^{18} exchanges between carbon dioxide molecules under the conditions of this study. (If a carbon sample is not present in the reactor O^{18} molecules exchange between carbon dioxide molecules at a negligible rate). A mixture of 92.0 per cent CO_2^{16-16} , 5.7 per cent CO_2^{18-18} , and 2.3 per cent CO_2^{16-18} (a non-equilibrium distribution of O^{18}) was introduced to the reaction system containing a 0.1 g cleaned carbon sample of 14.4 per cent burn-off Graphon at 500°C. The partial pressures of each carbon dioxide species were followed for 40 min. Fig. 2 gives the pressure changes and the change in the percentage CO_2^{16-18} during this time. The expected value of the percentage CO_2^{16-18} for a random distribution of O^{18} in the carbon dioxide, was calculated from the atom fraction of O^{18} in the carbon dioxide, $X = 0.069$, and Eq. (1)

$$\% CO_2^{16-18} = 100(2)(X)(1-X) \quad (1)$$

Eq. (1) is based upon setting the rate of formation of each carbon dioxide species proportional to the product of the appropriate atom fractions of oxygen. In the case of the formation of CO_2^{16-18} , its rate is multiplied by two (9).

The dashed line at the top of Fig. 2 gives the percentage CO_2^{16-18} for a distribution at isotopic equilibrium, that is 12.8 per cent. It is seen that the exchange did, indeed, proceed under the conditions used and that an

Table 1. Possible Reactions for the Formation of CO_2

- (a) $2CO + O_2 \rightarrow 2CO_2$
- (b) $2CO \rightarrow CO_2 + C$
- (c) $CO + C(O) \rightarrow CO_2 + C$
- (d) $CO + C(O)_i \rightarrow CO_2 + C$
- (e) $C(O)_i + C(O) \rightarrow CO_2 + C$
- (f) $2C(O) \rightarrow CO_2 + C$
- (g) $O_2 + 2C(O) \rightarrow 2CO_2$
- (h) $C + O_2 \rightarrow CO_2$, i.e. $C + O_2 \rightarrow C(O_2)_i \rightarrow CO_2$
- (i) $2C(O)_i \rightarrow CO_2 + C$, i.e. $2C + O_2 \rightarrow 2C(O)_i \rightarrow CO_2 + C$

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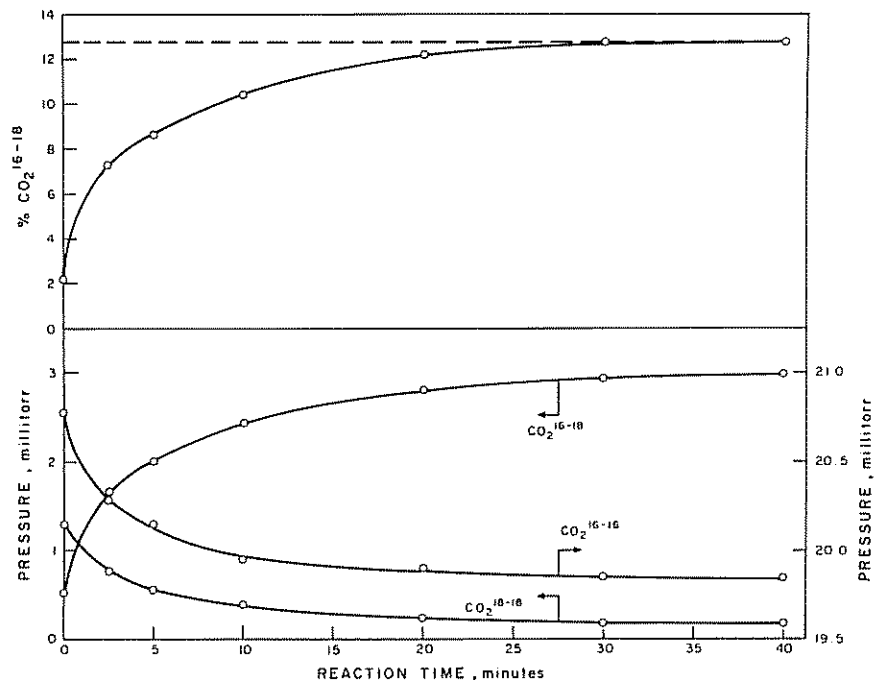


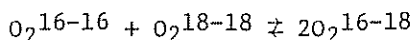
Figure 2. Oxygen Exchange Between CO₂ Molecules Over a Clean 14.4% Burn-off Graphon Surface at 500°C.

equilibrium distribution was achieved after about 30 min.

Since the exchange does take place, it was necessary to determine if the carbon dioxide was formed more rapidly than exchange could take place. If the exchange was faster than the rate of formation, an equilibrium distribution of O¹⁸ in the carbon dioxide would always result no matter what the reaction mechanism for carbon dioxide formation is. To determine this, a mixture of 95.8 per cent O₂¹⁸⁻¹⁸ and 4.2 per cent CO₂¹⁶⁻¹⁶ at a total pressure of 14.0 millitorr was reacted with a cleaned 14.4 per cent burn-off Graphon sample at 500°C. The results are given in Table 2. It can be seen that an equilibrium distribution of O¹⁸ was still not achieved after 30 min of reaction. (The value of X changed with time, since carbon dioxide was being produced as the reaction proceeded.) Therefore, O¹⁸ can be used to study the nature of the intermediate for carbon dioxide formation.

It was also noted that no O₂¹⁶⁻¹⁸ was produced during the interaction of O₂¹⁸⁻¹⁸ and CO₂¹⁶⁻¹⁶ with the carbon sample. Further, the exchange reaction:

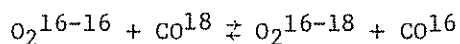
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did not proceed under the conditions used here.

Another possible exchange which would lead to an equilibrium distribution of O^{18} in the carbon dioxide is between stable surface oxide and gaseous carbon dioxide. However, no exchange was found at 500°C when CO_2^{16-16} was exposed to a surface on which $C(O^{18})$ had been formed previously on a 14.4 per cent burn-off sample at 500°C.

The reactions in Table 1 are now considered. Reactions (a), (b), (c) and (d) can be ruled out due to the results of the following experiment. Each of these reactions involves carbon monoxide. A mixture of CO^{18} (4.3 millitorr) and O_2^{16-16} (45.7 millitorr) were reacted with a cleaned 14.4 per cent burn-off Graphon sample at 500°C for 8 hr. Fig. 3 gives the results of this reaction. The pressure of CO^{18} remained essentially constant over the entire reaction period indicating that reactions (a)-(d) did not occur under these conditions. Therefore, none of these reactions are responsible for carbon dioxide formation. Here again, no O_2^{16-18} was produced; thus the reaction:



can be ruled out also under these conditions.

Reactions (e), (f) and (g) were also studied using O^{18} . Each of these reactions involves an interaction with the stable surface oxide, $C(O)$. Thus, $C(O^{18})$ was formed on a cleaned 14.4 per cent burn-off Graphon sample at 500°C by reacting the carbon with O_2^{18-18} . About 50 per cent of the

Table 2. Per Cent CO_2^{16-18} Formed by Exchange Between CO_2^{16-16} and CO_2^{18-18} During the Reaction of Graphon with a Mixture of CO_2^{16-16} and O_2^{18-18} at 500°C

Reaction time, min	Atom fraction of O^{18} in CO_2 (X)	Experimental % CO_2^{16-18} in CO_2	% CO_2^{16-18} Calculated by Eq. (1)
2.5	0.027	19.8	32.8
5	0.259	25.2	38.4
10	0.319	32.2	43.5
20	0.378	38.7	47.0
30	0.408	42.8	48.3

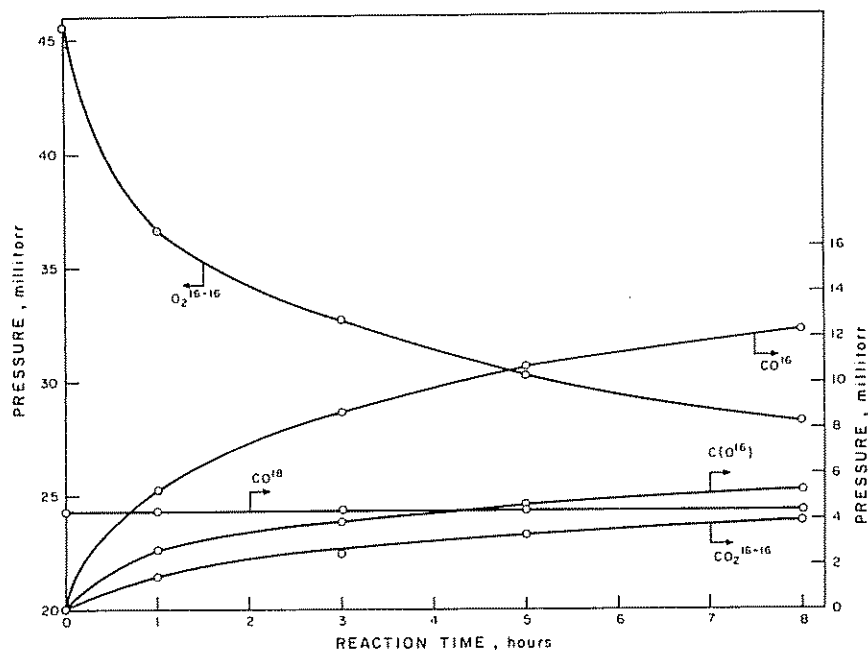


Figure 3. Plot of Reactants and Products for the Reaction of $O_2^{16-16} + CO^{18}$ with 14.4% Burn-off Graphon at $505^\circ C$.

active surface was covered. This sample was then reacted with O_2^{16-16} at $500^\circ C$. Fig. 4 presents the results of this reaction. The main carbon dioxide species produced was CO_2^{16-16} . CO_2^{18-18} was negligibly small; it could just be detected. Reactions (e) and (g) predict CO_2^{16-18} as the major species and (f) predicts the CO_2^{18-18} species to be the dominant one. Therefore, since O^{18} exchange can not be used to explain the observed results, all three of these reactions are ruled out as the major route of carbon dioxide formation.

Reactions (h) and (i) remain to be considered. These two reactions predict different distributions of O^{18} in the carbon dioxide produced, since we have shown that O^{18} exchange between the carbon dioxide molecules is slower than carbon dioxide formation. If a mixture of O_2^{16-16} and O_2^{18-18} is reacted with a cleaned Graphon sample, reaction (h) predicts the O^{18} distribution in the carbon dioxide would be the same as that in the oxygen. That is, only CO_2^{16-16} and CO_2^{18-18} would be produced and in the same ratio as in the oxygen. The slower O^{18} exchange would change this to an equilibrium O^{18} distribution, but at least initially

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it should not be at equilibrium. Reaction (i) predicts an equilibrium O^{18} distribution in the carbon dioxide at all times.

A mixture of 51.5 per cent O_2^{18-18} , 45.9 per cent O_2^{16-16} , and 2.6 per cent O_2^{16-18} was reacted with a cleaned 14.4 per cent burn-off Graphon sample at $500^\circ C$ and at a total starting oxygen pressure of 46.1 millitorr. Table 3 gives the percentages of the experimentally determined CO_2^{16-18} in the carbon dioxide formed along with the percentages predicted by reactions (h) and (i). Reaction (h) predicts just 2.6 per cent CO_2^{16-18} from the 2.6 per cent O_2^{16-18} in the oxygen mixture. The equilibrium distribution of CO_2^{16-18} predicted by reaction (i) is 49.8 per cent, calculated from eq. (1) where $X = 0.527$, as calculated from the oxygen mixture. It can be seen that the experimental value initially agrees almost exactly with that predicted by reaction (i) - an equilibrium distribution. The increase in the experimental CO_2^{16-18} percentage with time is attributed to the slow exchange of O^{18} in the carbon dioxide with O^{16} in the quartz reaction tube. Since the production of CO_2^{16-18} from the CO_2^{16-16} and CO_2^{18-18} which are produced is too slow to explain these results, it is concluded that reaction (i) is responsible for the formation of carbon dioxide. That is, carbon dioxide is a primary product of the interaction of

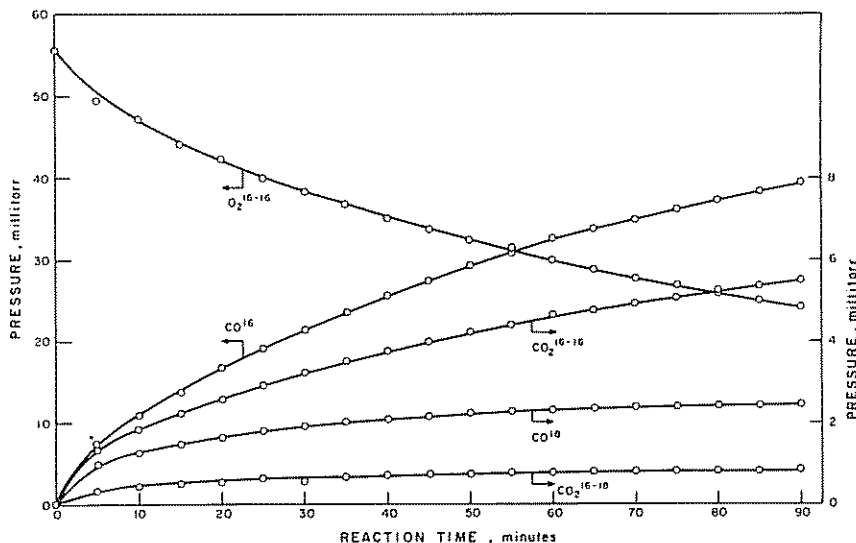


Figure 4. Typical Reaction Between O_2^{16-16} and Graphon Which had a Fraction of its Surface Covered with O^{18} Oxide.