Absolute Rates of the Carbon-Carbon Dioxide Reaction

The etch-decoration transmission electron microscopy technique was used to measure the turnover frequencies of the C-CO_2 reaction in the temperature range 600–900°C. The absolute rate constants of the elementary rate steps were determined, and were in reasonably good agreement with statistical theories. The rates on monolayer steps of graphite were higher than those on multilayer steps by approximately four orders of magnitude at 800°C, because the C-O bond in the reaction intermediate is stronger by about 9 kcal/mol on the monolayer steps. The rates of vacancy formation in the lattice were also determined. The vacancies are formed by atomic oxygen dissociated from CO_2.

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SCOPE

The carbon-carbon dioxide reaction is a basic reaction important in all combustion and gasification processes for fossil fuels, as well as in metallurgical and other industrial processes. All previous investigations on the kinetics of this reaction were conducted by measuring weight changes in the carbon or by evolved gas analysis, and rates averaged over all crystallographic faces were reported.

In this study the technique of etch-decoration transmission electron microscopy was used to measure the specific rates of gasification of carbon on well-defined active sites on a single-crystal graphite sample. The data on such rates, expressed as turnover frequency, provide more insights into the fundamental processes taking place on the surface of carbon. Turnover frequency also serves as a potential tool for correlating the voluminous but widely different literature data on gasification rates of various types of carbon.

CONCLUSIONS AND SIGNIFICANCE

The turnover frequencies for the C-CO_2 reaction were measured in the temperature range 600–900°C. The Langmuir-Hinshelwood rate equation was satisfactorily obeyed, and the absolute rate constants for the elementary rate steps were determined. These fundamental constants may be interpreted reasonably well by statistical theories.

The turnover frequency on the monolayer edge carbon for the C-CO_2 reaction is substantially higher than that on the multilayer edges, by approximately four orders of magnitude at 800°C. This is contrary to the case for the C-O_2 reaction. The reason for the high rates on the monolayer edge is that the bond energy between C and O in the intermediate oxygen complex is mugh higher, by about 9 kcal/mol calculated from our rate data, than that on the multilayer edge.

The rates of vacancy formation in the graphite lattice were also measured in the above temperature range. The formation of vacancies is an important step in the overall gasification rate at higher temperatures. It is concluded that atomic oxygen generated by thermal dissociation of CO_2 is the species responsible for vacancy formation because the probabilities for successful collision of 0 atoms for forming a vacancy are the same for all three gas-carbon reactions with O_2, H_2O and CO_2, regardless of the molecular precursor, and the rate of vacancy formation is drastically lowered by the addition of CO in CO_2.

INTRODUCTION

The C-CO_2 reaction giving 2CO has been one of the most intensively investigated because of its scientific as well as technological importance. It is a basic reaction in combustion and gasification of coal and other fossil fuels, and in metallurgical and other industrial processes. The following Langmuir-Hinshelwood rate equation has been found to fit experimental data for carbon reactants ranging from dirty coal chars to high-purity single-crystal

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graphite (Walker et al., 1959; Gadsby, et al., 1948; Lewis et al., 1949; Bonner and Turkevich, 1951; Strange and Walker, 1976):

$$\text{Rate} = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO} + k_3 P_{CO_2}} \tag{1}$$

which can be derived from the most accepted form of the Langmuir-Hinshelwood mechanism:

$$C_f + CO_2 \underset{j_1}{\overset{i_1}{\rightleftarrows}} C(O) + CO(g) \tag{2}$$

$$C(O) \xrightarrow{j_3} CO(g) \tag{3}$$

The rate constants in Eq. 1 are related to the elementary rate constants by: $k_1 = i_1$, $k_2 = j_1/j_3$, and $k_3 = i_1/j_3$.

The rates of all previous studies on this reaction were measured by changes of mass or evolved gas analysis, and hence were the total rates over all active sites, which are edges and defects on the surface in the temperature ranges of these studies. Until the study by Strange and Walker (1976), all previous workers used poorly defined carbons, such as coconut shell charcoal, coal coke, electrode graphite, etc. Besides the effects of impurity and mass transfer limitations, the active sites were not known in these studies. (The number of active sites can, however, be indirectly determined by chemisorption of O_2, as shown by Laine et al., 1963.) In the study by Strange and Walker (1976), a high-purity, well-defined single-crystal graphite—SP 1—was used in the form of flakes about 0.4 μm in thickness and 30 μm in diameter. The active sites were predominantly on the peripheral edges, thus one may calculate rates on a per active site basis. Such a rate is termed turnover frequency.

Since the invention of the technique of etch-decoration electron microscopy by Hennig (1966), the direct measurement of turnover frequency on the single-crystal graphite surface has become possible. This technique has proved valuable for studying gas-carbon reactions, both uncatalyzed and catalyzed, by several groups and in our laboratory (Yang, 1983). It is felt that a measurement of the absolute rate constants of the C-CO_2 reaction and a critical evaluation of the Langmuir-Hinselwood mechasism can now be made by this technique.

EXPERIMENTAL

The technique of etch-decoration electron microscopy has been fully described elsewhere (Hennig, 1966; Wong, 1983; Yang, 1983). It consists of: cleaving crystals (natural graphite from Ticonderoga, NY) to a thickness of a few hundred angstroms; etching the graphite in CO_2, which expands surface vacancies to create pits one atomic layer deep; decorating the edge of the pits with gold nuclei; and examining the sample with a transmission electron microscope (TEM). The radius or the size of a pit is proportional to the time of etching. The atoms on the edge of the pit are the active sites. From the pit growth rate, we are able to calculate the turnover frequency in terms of the number of carbon atoms removed per active site per unit time, via

$$r\left(\frac{\text{atoms gasified}}{\text{edge atom} \cdot s}\right) = \frac{\rho_{0001} 2\pi R dR/dt}{\rho_{edge} 2\pi R H},$$

where $\rho_{0001} = 0.377$ C/Å^2, $\rho_{edge} = 0.120$ C/Å^2, and H = step height = 3.35 Å for graphite. When linear R-t plots are obtained, as will be discussed, dR/dt is constant, and the turnover frequency may be evaluated directly from the electron micrograph.

In studying the C-CO_2 reaction, precautions must be taken in removing traces of O_2 from CO_2 and the "inert" carrier gas. The ratio of the overall rates, as measured by TGA or evolved gas analysis (for all crystallographic planes of graphite) for the O_2/CO_2 reactions is approximately 10^5 under conditions usually reported in the literature (Walker et al., 1959). Thus, the gasification rate by 1 ppm of O_2 is approximately the same as the rate by 0.1 atm (10.1 kPa) of CO_2; most of the commercial grades of the inert gases, e.g., N_2 and Ar, and CO_2, contain more than 1 ppm of O_2. In this study an "Oxygen-Free" grade N_2 (<0.5 ppm O_2, Linde) was used as the carrier gas. The CO_2 was "Aquarator Grade" with a minimum purity of 99.99%, and the CO was "Grade F" with a minimum purity of 99.97%, both supplied by Linde Division of Union Carbide Company. The gas mixture was further purified by flowing through a preheater column packed with copper turnings maintained at 550°C to remove the residual O_2 in the gas stream. Oxidation of copper turnings by CO_2 is undetectable at this temperature as concluded from our TGA measurements. In addition, a drierite column was used to remove moisture in the gas mixture before the gas entered the reactor.

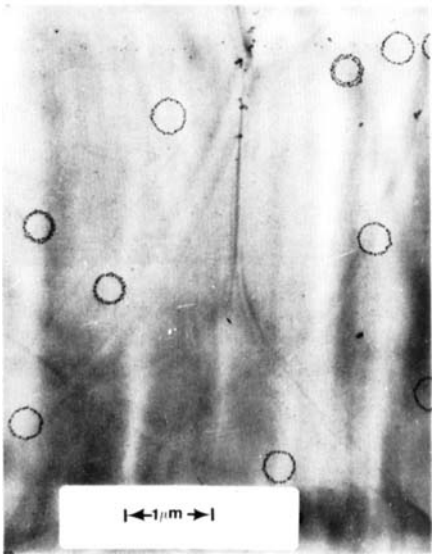

Figure 1. Transmission electron micrograph of monolayer etch pits on basal plane of graphite crystal decorated by gold nuclei. The graphite was etched by 0.8 atm (81.1 kPa) CO_2 at 700°C for 65 min.

For evaluating the three rate constants, and as a test of the rate equation, Eq. 1, the equation may be inverted,

$$\frac{1}{\text{rate}} = \frac{k_3}{k_1} + \frac{k_2}{k_1}\frac{P_{CO}}{P_{CO_2}} + \frac{1}{k_1}\frac{1}{P_{CO_2}} \tag{5}$$

Two series of experiments were done: in method 1, P_{CO_2} was varied while CO was absent, so k_1 and k_3 could be evaluated; in method 2, P_{CO}/P_{CO_2} was varied while P_{CO2} was held constant, so k_2 could be measured.

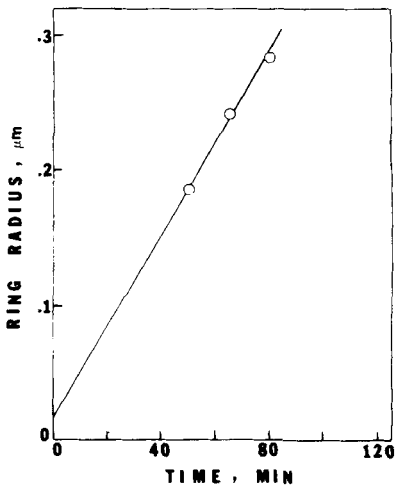

Figure 2. Plot of pit size as a function of time of etching with 0.8 atm (81.1 kPa) CO_2 at 700°C.

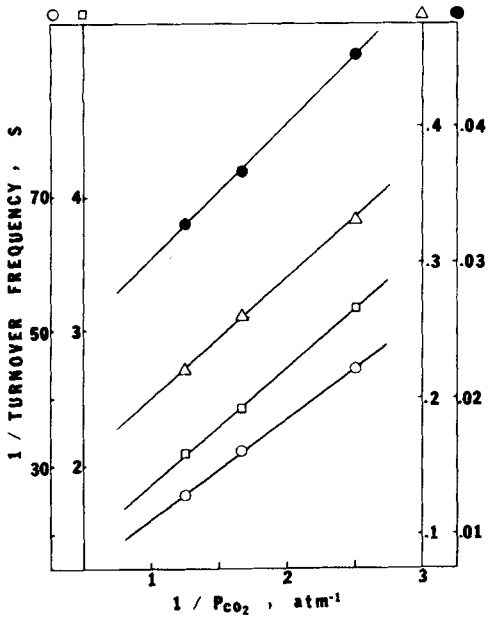

Figure 3. Dependence of turnover frequency for carbon gasification on the partial pressure of CO_2 with no CO addition at various temperatures: 600°C (○); 700°C (□); 800°C (△); 900°C (●).

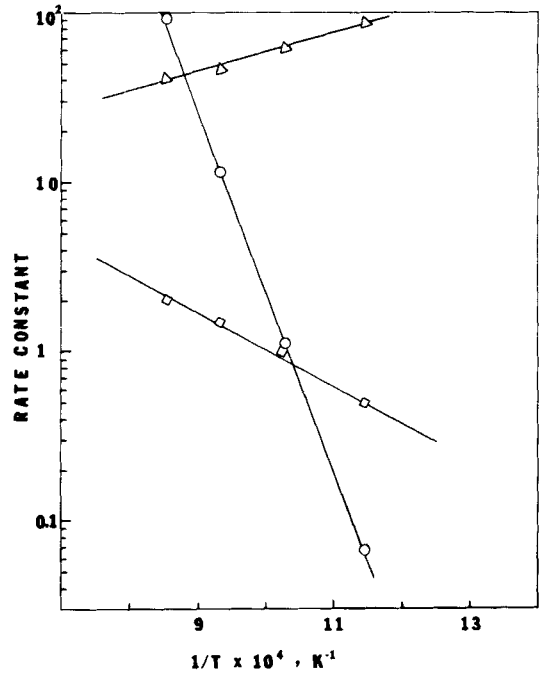

Figure 5. Langmuir-Hinshelwood rate constants for the C-CO_2 reaction: k_1 in $atm^{-1}s^{-1}$ (○); k_2 in atm^{-1} (△); k_3 in atm^{-1} (□).

Experimental runs were made at a total pressure of 1 atm (101.3 kPa) and temperatures in the range 600–900°C. In method (1) P_{CO_2} was varied from 0.4 to 0.8 atm (40.5-81.1 kPa). In method (2) P_{CO_2} was held at 0.4 atm (40.5 kPa) while P_{CO}/P_{CO_2} was varied from 0.2 to 0.8 atm (20.3-81.1 kPa). Proper lengths of reaction time (8 min to 8 h) were used to yield etch pits of sizes of approximately 0.1 to 1 μm, which were found most suitable for gold decoration and TEM examination.

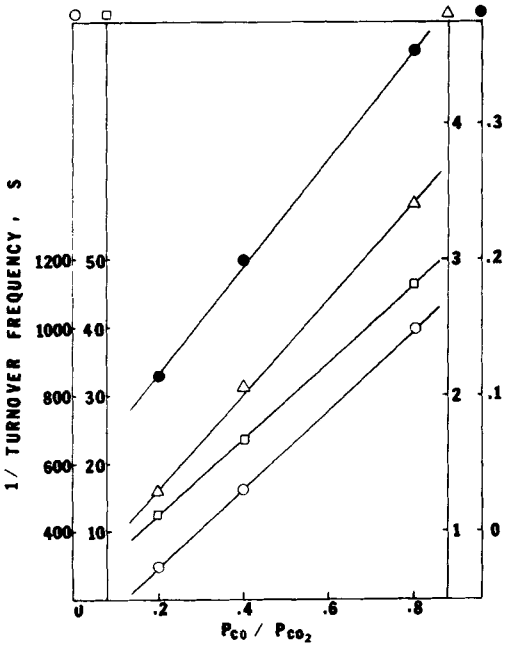

Figure 4. Dependence of turnover frequency for carbon gasification on the ratio P_{CO}/P_{CO_2} at P_{CO_2} at = 0.4 atm (40.5 kPa) for various temperatures: 600°C (○); 700°C (□); 800°C (△); 900°C (●).

RESULTS AND DISCUSSION

A typical transmission electron micrograph of the gold decorated basal plane of graphite etched by CO_2 is shown in Figure 1. Like the C-O_2 reaction, all etch pits created by CO_2 are circular. The pits etched by H_2O without catalysts (Duan and Yang, 1984; Yang and Wong, 1983) and by O_2 with transition metal carbides (Yang and Wong, 1984) are all hexagonal, consisting of zigzag or $\{10\bar{1}0\}$ faces. But unlike the C-O_2 reaction, the pits are unusually uniform in size, which indicates the absence of the chemisorption/surface diffusion mechanism (Yang and Wong, 1981a; 1981b). Thus all gasification events for the C-CO_2 reaction are caused by direct collision of CO_2 on the edge carbon atoms which are the active sites. The turnover frequency calculated from Figure 1 is 0.51 atom/atom/s. Figure 2 shows a plot of the radius of pits as a function of time of reaction. The linear dependence of the radius with time made it possible to determine the turnover frequency from one data point in the subsequent runs. The small positive intercept in Figure 2 was also observed for the C-O_2 reaction by earlier workers (Evans and Thomas, 1971; Hennig 1964) which was attributed to higher rates in the early stage when the pits were very small.

Absolute Rate Constants and a Test of the Langmuir-Hinshelwood Rate Equation

Plots of the data according to experimental methods 1 and 2 can provide a test of the fitness to the Langmuir-Hinshelwood rate equation, and if acceptable, can subsequently be used to determine the absolute rate constants.

Figure 3 shows satisfactory linear plots for reciprocals of turnover frequencies vs. reciprocals of CO_2 partial pressures at $P_{CO} = 0$. Figure 4 presents good linear plots for reciprocals of turnover frequencies against P_{CO}/P_{CO_2} at $P_{CO_2} = 0.4$ atm (40.5 kPa; constant). From the plots in Figures 3 and 4, k_1, k_2 and k_3 have been calculated as shown in Figure 5. These plots show that the Langmuir-Hinshelwood rate equation indeed fits the data. The data were analyzed using a nonlinear (polynomial) regression analysis

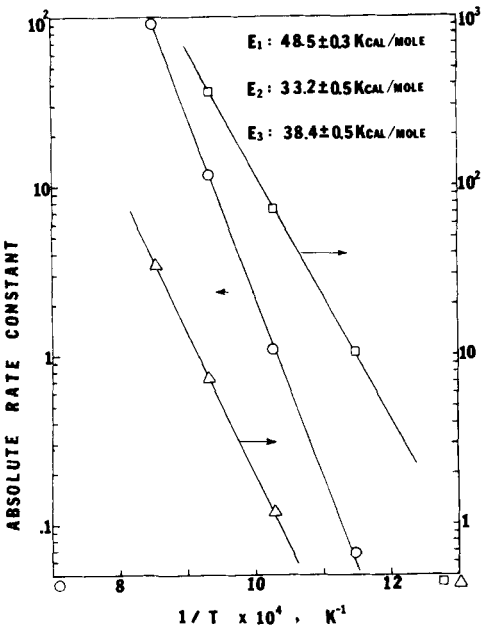

Figure 6. Absolute rate constants for the C-CO_2 reaction: i_1 in $atm^{-1}\cdot s^{-1}$ (○); j_1 in $atm^{-1}\cdot s^{-1}$ (□); j_3 in s^{-1} (△).

to yield the following rate constants with their respective confidence boundaries and variances (S^2):

$$k_1 = (9.07 \pm 1.0) \times 10^{10} \exp(-48{,}500 \pm 300)/RT \text{ s}^{-1} \cdot \text{atm}^{-1}; \quad S^2 = 0.0265$$

$$k_2 = (4.364 \pm 0.075) \exp(5{,}241 \pm 60)/RT \text{ atm}^{-1}; \quad S^2 = 0.000213$$

$$k_3 = (185 \pm 30) \exp(10{,}240 \pm 350)/RT \text{ atm}^{-1}; \quad S^2 = 0.0255$$

The values of the three elementary rate constants, i_1, j_1, and j_3, were then calculated directly from the above rate constants, and are shown in Figure 6 as well as below:

$$i_1 = (9.07 \pm 1.0) \times 10^{10} \exp(-48{,}500 \pm 300)/RT \text{ s}^{-1} \cdot \text{atm}^{-1}$$

$$j_1 = (2.14 \pm 0.5) \times 10^{9} \exp(-33{,}200 \pm 500)/RT \text{ s}^{-1} \cdot \text{atm}^{-1}$$

$$j_3 = (4.85 \pm 1.0) \times 10^{8} \exp(-38{,}400 \pm 500)/RT \text{ s}^{-1}$$

These rate constants may be interpreted in terms of statistical or absolute rate theory as follows. In the forward reaction in Reaction 2, we assume the CO_2 molecule is not localized in the adsorbed and activated state, and hence it possesses two degrees of translational freedom. Thus the frequency factor for i_1 is

$$i_{1o} = \frac{5 \times 10^{13}}{RT} \frac{kT}{h} \frac{F\ddagger}{F_{CO_2} f_s} = \frac{5 \times 10^{13}}{RT} \frac{kT}{h} \frac{h}{(2\pi mkT)^{1/2}} \frac{b\ddagger}{b_{CO_2}} \tag{6}$$

where $F\ddagger$ is the partition function of the activated CO_2 on the active site with $kT/h\nu$ factored out, or with one less degree of vibrational freedom; F_{CO_2} and f_s are the partition functions of $CO_2(g)$ and active site, respectively. The quantities denoted by b contain a partition function for rotational and vibrational ($b\ddagger$ has no vibrational) degrees of freedom for the activated and gas-phase CO_2. Equation 6 contains no concentration of active sites because i_{1o} is expressed on a per active site basis. The value of f_s is taken as unity, since the surface carbon atom has no translational or rotational degrees of freedom and can undergo only very restricted vibration. It is further assumed that the adsorbed and activated CO_2 has two degrees of rotational freedom, as does the gas-phase CO_2, we have

$$\frac{b\ddagger}{b_{CO_2}} \cong 1 \tag{7}$$

Here the vibrational factor for gas-phase CO_2 is near unity. Thus, the calculated value for the frequency factor is

$$i_{10} = 1.05 \times 10^7 \text{ cm}^2 \cdot \text{N}^{-1} \cdot \text{s}^{-1}$$

which compares rather reasonably with the experimental value of 8.95×10^9 $cm^2 \cdot N^{-1} \cdot s^{-1}$. This calculation and comparison indicate that the activated CO_2 should indeed be mobile on the carbon surface, because otherwise the calculated frequency factor would have to be lowered by a factor of 10^{9-18} from the above value.

Similar calculations may be made for the reverse reaction of Reaction 2. The frequency factor for the reverse reaction, j_{1o}, can be calculated by assuming (a) the adsorbed and activated CO is not localized, and (b) the chemisorbed 0 or C(O) is treated as a localized active site. The calculated value is

$$j_{10} = 1.30 \times 10^7 \text{ cm}^2 \cdot \text{N}^{-1} \cdot \text{s}^{-1}$$

which is in good agreement with the experimental value of 2.11×10^7 $cm^2 \cdot N^{-1} \cdot s^{-1}$. In the above calculations it is assumed that the activated state does not contain a rotational factor. If two degrees of rotational freedom are assumed for the activated complex, however, as for some surface reactions (Laidler, 1965), we would have

$$j_{10} = \frac{5 \times 10^{13}}{RT} \frac{kT}{h} \frac{h}{(2\pi mkT)^{1/2}} \frac{h^2}{8\pi^2 IkT} \tag{8}$$

where I is the moment of inertia of CO. The calculated value would be 3.30×10^4 $cm^2 \cdot N^{-1} \cdot s^{-1}$ which is substantially lower than the experimental value.

The frequency factor for the net gasification reaction, C(O) → CO, is given by statistical theory as

$$j_{30} = \frac{kT}{h} \tag{9}$$

assuming that both the activated complex and C(O) species are rigidly held and the ratio of the partition functions is unity. Thus the frequency factor is simply the vibrational frequency of the thoroughly excited state of the C-C bond, which is about 2×10^{13} s^{-1} in our temperature range. This frequency is however, for breaking of only one C-C bond; whereas, for the reaction to occur two C-C bonds, planar at 120° apart from the C-O bond, must be broken simultaneously. The requirement for the correlated vibration of the two C-C bonds should further lower the value for j_{30} from that for one bond. The experimental value of 4.9×10^7 s^{-1} is not unreasonable. In fact, as seen in Table 1, all previous workers except Strange and Walker reported a j_{30} value substantially lower than 10^{13} s^{-1}, in agreement with the above discussion.

Comparison of Rates on Multilayer and Single-Layer Edges

The active sites on carbon for gas-carbon reactions under normal conditions are the atoms with a free sp^2 electron, which are the surface atoms located on edges and defects. In all previous studies the rates were measured by either TGA or evolved gas analysis, both giving the total rates over all edges. The total rates were thus contributed by predominantly multilayer edges. The rates measured in this study, on the contrary, are rates on the monolayer edges or steps.

For the C-O_2 reaction, the rate on the multilayer edge is about a hundred times higher than that on the monolayer edge (Evans and Thomas, 1971). This enhancement phenomenon was termed

TABLE 1. COMPARISON OF ELEMENTARY KINETIC PARAMETERS FOR THE C-CO_2 REACTION

Carbon	i_{1o} $s^{-1}\cdot atm^{-1}$*	E_1 kcal/mol	i_{2o} $s^{-1}\cdot atm^{-1}$*	E_2 kcal/mol	i_{3o} s^{-1}	E_3 kcal/mol	Reference
Pitts. bitum. coal coke	5.93×10	28.4	8.37×10^7	58.6	5.7×10^8	65.0	Johnson
Spheron No. 6 Carbon Black	2.57×10^4	53.0	7.76×10^1	36.0	8.58×10^5	58.0	Menster & Ergun
SP-1 graphite	1.2×10^{17}	99.0	3.2×10^{13}	74.0	4.35×10^{13}	87.0	Strange & Walker
Coconut charcoal	4.5×10^9	76.0	2.72×10^{11}	76.0	1.88×10^{12}	76.0	Blackwood & Ingene
Act. carbon	—	—	—	—	1.43×10^7	59.0	Ergun
Ceylon graphite	—	—	—	—	1.58×10^5	59.0	Ergun
Coke	1.3×10^5	47.6	9.20×10^3	38.9	6.58×10^5	53.9	Lewis et al.
Anthracite	4.3×10^2	32.5	1.13×10^3	32.2	2.45×10^5	49.1	Lewis et al.
This work	9.07×10^{10}	48.5	2.14×10^8	33.2	4.85×10^7	38.4	—

* SI conversion: kPa = atm × 101.325.

"cooperative effect." It has been suspected, by comparing the ratio of rates for reactions with $O_2/H_2O/CO_2$ on multilayer and single-layer edges, that the cooperative effect does not exist for reactions with H_2O and CO_2 (Yang and Wong, 1983). With the data obtained in this study, it is now possible to make a direct comparison between the two rates for the CO_2 reaction.

Strange and Walker (1976) reported TGA rates for a well-defined graphite sample in the temperature range 902–1,007°C. The sample was of high purity and was single-crystal discs with well-defined multilayer edges, which were the active sites for the reaction. A direct comparison can be made between their rates at 902°C and our rates at 900°C. The rate constants, in (this study)/(Strange and Walker), are approximately: for k_1, 99/0.05; k_2, 41/200; and k_3, 2/20, all in units containing atm and s, with the constants of Strange and Walker having been converted into C atoms removed per C active site. The turnover frequency on the monolayer edge is thus about four orders of magnitude higher than the turnover frequency on multilayer edges as reported by Strange and Walker.

A direct comparison of our data on single-layer edges with previous data, as shown in Table 1, is not possible, since the fraction of edge planes on the surface was not defined in the other studies. However, it is apparent from Table 1 that our rates, mainly k_1, are higher than all reported rates by several orders of magnitude, because the fraction of edges in their samples was not likely lower than that of SP-1 graphite, which is a rather large crystal.

From the above comparison, it is clear that the "cooperative effect" for the C-CO_2 reaction is in the opposite direction, i.e., the turnover frequency on monolayer edges is much higher than that on multilayer edges, contrary to the C-O_2 reaction. Although the cooperative effect for the C-O_2 reaction is not understood (Evans and Thomas, 1971), it is possible to explain the reverse effect on the C-CO_2 reaction based on thermochemical considerations as discussed below.

Although the precise nature of the C(O) species in the Langmuir-Hinshelwood mechanism is not known, it is possible to estimate the bond strength between carbon and oxygen in this species from the kinetic data. The heat of reaction of the oxygen exchange reaction, i.e., $C_f + CO_2 \rightleftarrows C(O) + CO$, is $E_1 - E_2$, which is equal to 15.3 kcal/mol endothermic. The bond energy between C and O in C(O) can be calculated, since the bond to be formed (in CO) and the bond to be broken (in CO_2) are both known. However, the formation of C(O) on the edge carbon involves some localization of a π-electron from the graphite, which results in a loss of C-C bond energy within the graphite as shown by Walker et al. (1965). The bond energy in C(O) can thus be estimated by considering these three energies. Based on a heat of reaction for the oxygen exchange reaction of 25 kcal/mol endothermic, Strange and Walker (1976) estimated that the C(O) bond has two-thirds double bond character. Their value is for the oxygen chemisorbed on the multilayer edge. Our value for the heat of reaction of 15.3 kcal/mol ($E_1 - E_2$) indicates that the C(O) bond on the monolayer edge is about 9.7 kcal/mol stronger than that on the multilayer edge. The stronger C(O) bond is apparently the reason for the easier breakage, and hence the higher rate, of C(O) from the graphite (with two C-C bonds).

The substantially higher rates of the CO_2 reaction on the monolayer edge as compared with that on the multilayer edge can thus be attributed to the stronger bond between C and O in the oxygen complex on monolayer edges. The higher rates cannot be attributed to impurities (or catalysts) because most of the carbon samples listed in Table 1 contained considerably more impurities than the graphite sample used in this study, and the effect is reversed for the C-O_2 reaction.

The monolayer edge and multilayer edge represent two extreme types of active sites for the gas-carbon reactions. The "cooperative effect" in the C-O_2 reaction is likely a gradual one depending on the number of layers forming the edge as seen in our laboratory (Wong and Yang, 1982). The dependence of reactivity on the number of layers forms the basis for the familiar compensation effect, i.e., the frequency factor and the activation energy for a given surface reaction usually increase or decrease together. The compensation effect for the C-CO_2 reaction is evident in Table 1. Our interpretation of the compensation effect is in accord with Sosnovsky's (1959) theory on catalytic reactions.

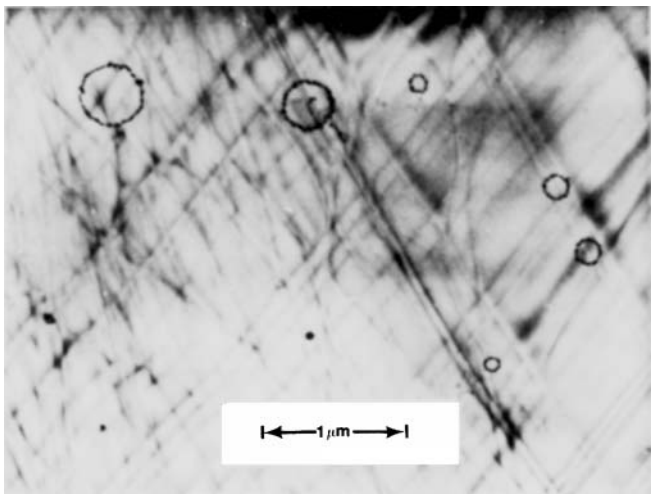

Figure 7. Transmission electron micrograph of gold-decorated etch pits on graphite etched by CO_2 showing new pits originated from newly formed vacancies.

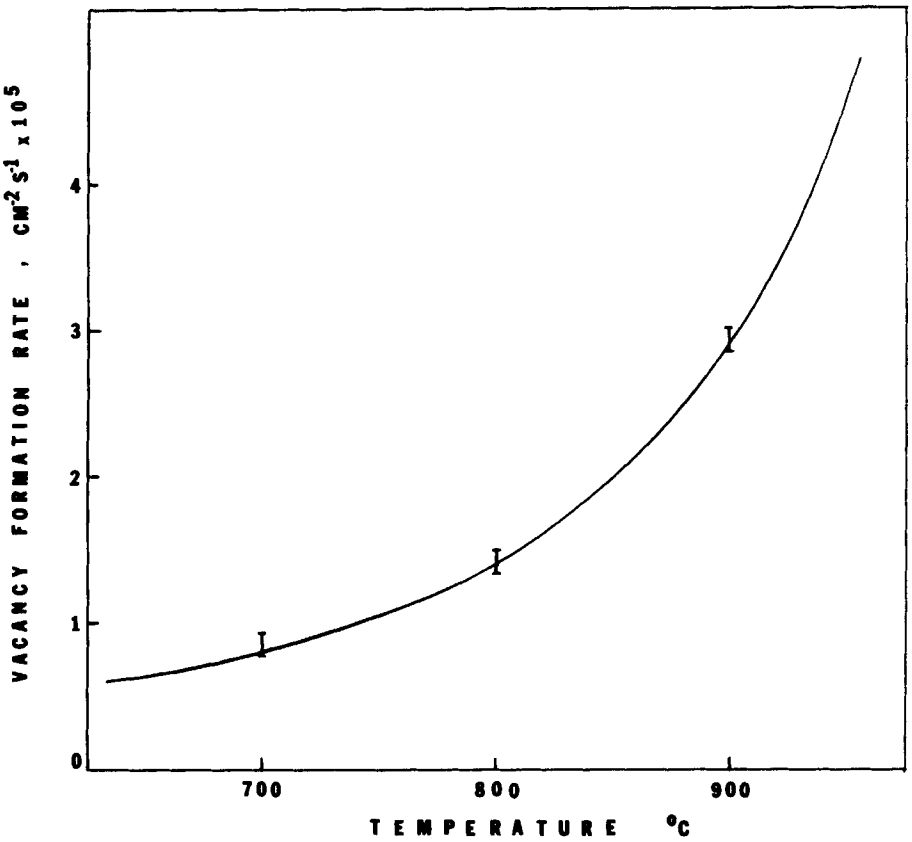

Figure 8. Rate of vacancy formation in graphite lattice at 900°C in 0.4 atm (40.5 kPa) pressure of CO_2 with no CO addition.

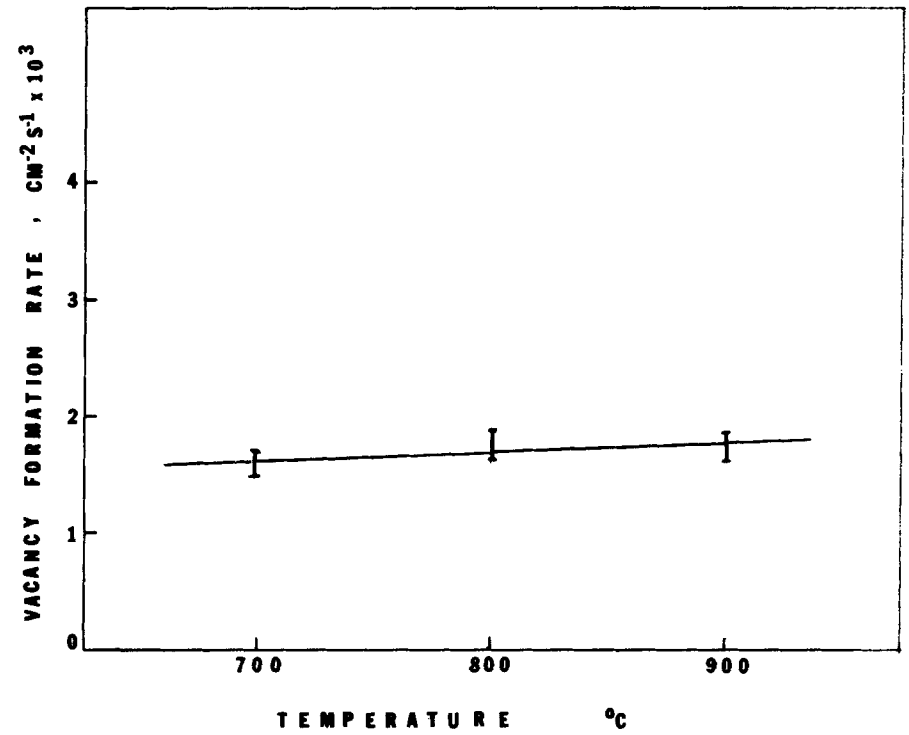

Figure 9. Rate of vacancy formation in graphite lattice at 900°C in 0.4 atm (40.5 kPa) P_{CO_2} and $P_{CO}/P_{CO_2} = 0.4$.

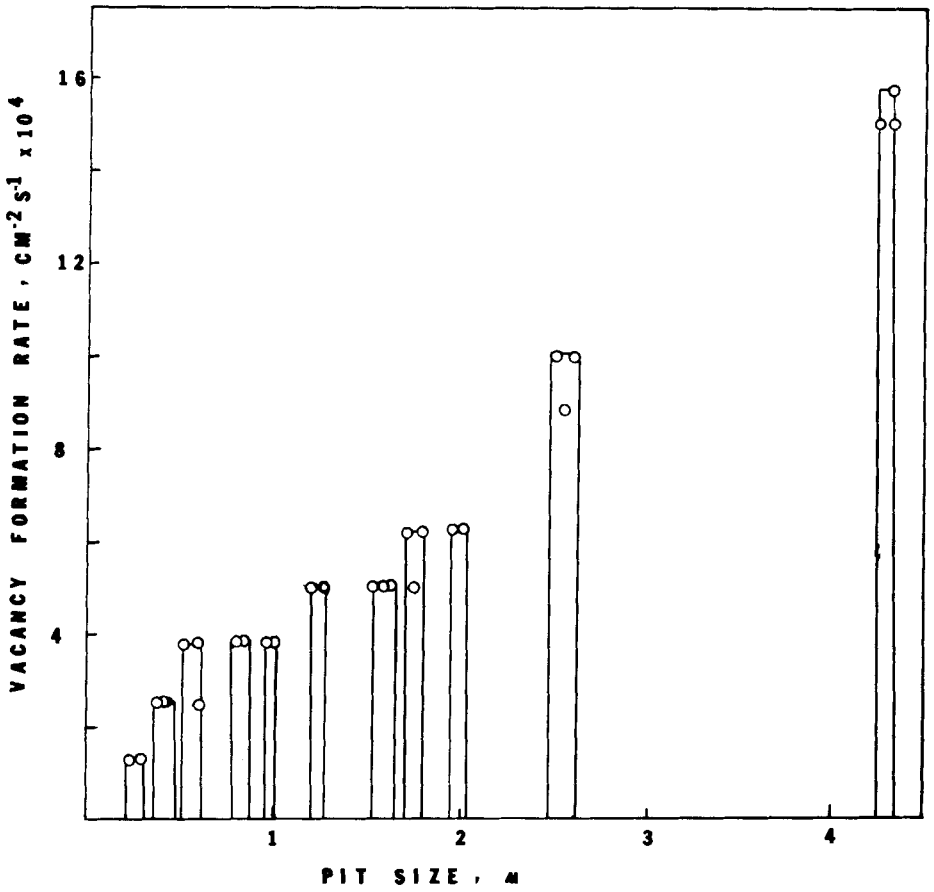

Figure 10. Dependence of vacancy formation rate in graphite lattice in 0.4 atm (40.5 kPa) of CO_2 at 900°C on the time of reaction (which is proportional to pit size).

Rate and Mechanism of Vacancy Formation

In gas-carbon reactions two concurrent surface processes take place: (a) removal of edge carbon atoms on both multilayer edge and monolayer edge, and (b) abstraction of carbon atoms within the basal plane, followed by the formation and expansion of new pits. Vacancy formation refers to the second process. It is known that the second process is much slower than the first and contributes relatively little to the overall rate. It is important, however, to understand this process because it becomes important at higher temperatures. Hennig (1964) and Evans and Thomas (1971) have measured the rate of vacancy formation for the C-O_2 reaction. Duan and Yang (1984) have measured the rate of vacancy formation for the C-H_2O reaction and have shown that if 0 atoms formed by thermal dissociation are responsible for vacancy formation, the probabilties of successful collision for forming a vacancy are the same for both O_2 and H_2O reactions, regardless of the original source of the 0 atoms.

The rate of vacancy formation for the C-CO_2 reaction is determined by the number of pits with radii smaller than those of the largest pits. The largest pits are uniform in size and originate from the inherent vacancies. The smaller pits, with varying sizes, are from the vacancies formed during the reaction. A typical micrograph of pits formed from new vacancies is shown in Figure 7. It is also possible to determine from such micrographs the rate of vacancy formation as a function of reaction time.

The rate of vacancy formation was measured for temperature of 600–900°C. Like the reactions with O_2 and H_2O, the abstraction of basal plane atoms becomes vigorous only at temperatures above about 700°C. Figures 8 and 9 present, respectively, the rates of vacancy formation at 900°C for CO_2 = 0.4 atm (40.5 kPa) (without CO) and for 0.4 atm CO_2 with $P_{CO}/P_{CO_2} = 0.4$ (at a total pressure of 1 atm or (01.3 kPa). With even a very small amount of CO addition, the rate of vacancy formation is drastically lowered. In such cases it becomes very difficult to determine the rate, because a very large surface is needed.

The above data can be accounted for from kinetic considerations by assuming that the O atoms dissociated from CO_2 are responsible for the abstraction. The equilibrium concentration of O atoms for the thermal dissociation

$$CO_2 \rightleftarrows CO + O \tag{10}$$

is

$$[O] = 14{,}370\sqrt{[CO_2]}e^{-64{,}820/RT}\ (\text{atm}) \tag{11}$$

where concentrations are in atm. The probability of abstraction of a carbon atom upon each collision by an O atom is

$$\begin{aligned}\epsilon &= \text{rate of pit formation/collision frequency} \\ &= 1.13 \times 10^{-10}(700°C);\ 1.81 \times 10^{-10}(800°C);\ 3.82 \times 10^{-10}(900°C)\end{aligned} \tag{12}$$

which yields an activation energy of 13.7 kcal.

The values of ϵ calculated for the C-O_2 and the C-H_2O reactions (Duan and Yang, 1984) are very close to the above values for the

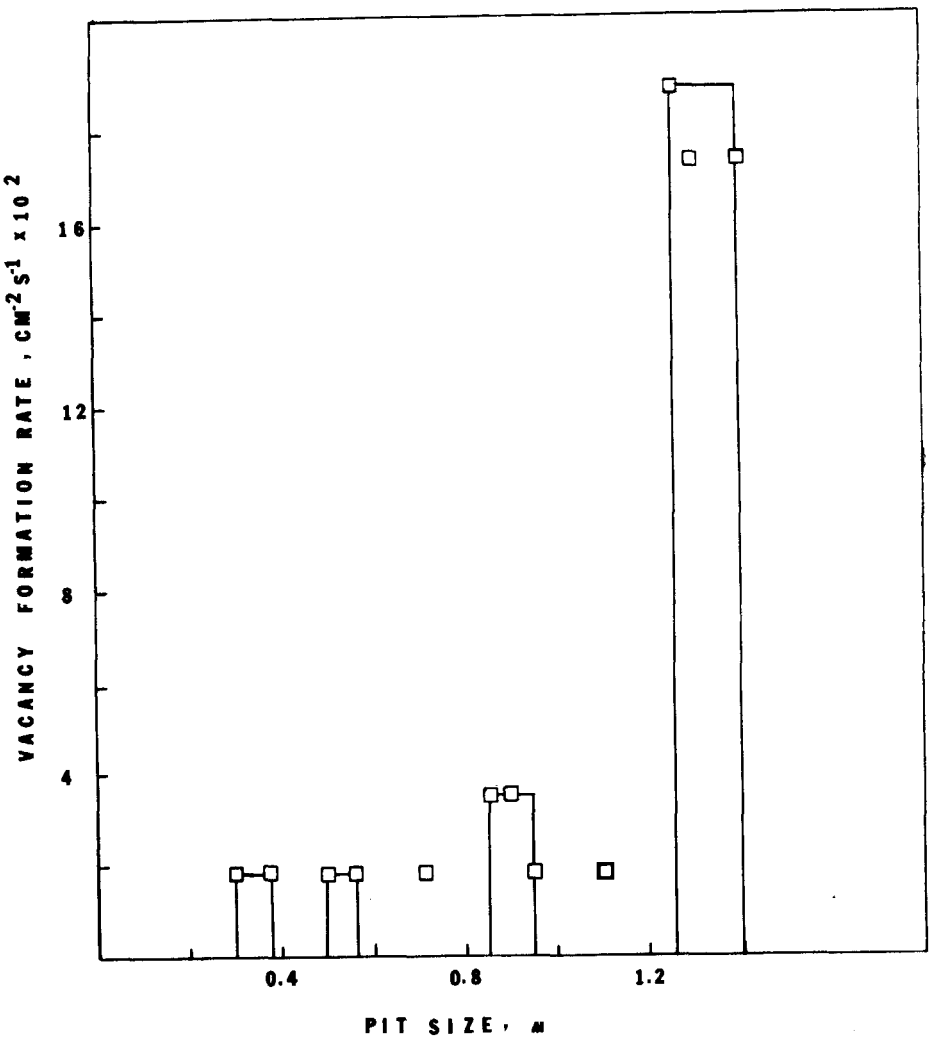

Figure 11. Dependence of vacancy formation rate in graphite lattice on reaction time at 900°C with 0.4 atm (40.5 kPa) CO_2 and $P_{CO}/P_{CO_2} = 0.4$.

C-CO_2 reaction, which is strong evidence that O atoms, regardless of their origin, are responsible for vacancy formation. Furthermore, with the addition of CO, the concentration of O atoms is drastically reduced in Reaction 10, which results in the observed reduction of the vacancy formation rate.

Figures 10 and 11 show, respectively, without and with CO addition to CO_2, the rate of vacancy formation as a function of reaction time. The reaction time is expressed by pit size because of their linear relationship. It is seen that with CO addition the rate of vacancy formation is independent of time whereas without CO the rate decreases with time. For the reaction without CO, O atoms strongly adsorb on the basal plane of graphite; they accumulate on the surface with time and hence retard the abstraction reaction. This interpretation is hence consistent with all data presented above. With the addition of CO, the equilibrium concentration of O is practically zero, and the abstraction of C atoms from the basal plane is likely due to the mechanism shown in Eqs. 2 and 3, i.e., resulting directly from the collision of CO_2 on the basal-plane atom. From the above data, the ratio of the ϵ values for CO_2/O is approximately 5×10^{-12} at 800°C.

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NOTATION

b	= rotational and vibrational factor
C_f	= free active site on carbon
C(O)	= chemisorbed oxygen
E	= activation energy
$F\ddagger$	= partition function for activated complex excluding the vibration mode.
F	= partition function for gas molecule.
f_s	= partition function for active sites
H	= step height
h	= Plank's constant
I	= moment of inertia
i_1, j_1, j_3	= absolute rate constants in Eqs. 2 and 3
k	= Boltzman constant
k_1, k_2, k_3	= Langmuir-Hinshelwood rate constants in Eq. 1
m	= mass of gas molecule or complex
[O]	= equilibrium concentration of oxygen atom
P	= total or partial pressure
R	= gas constant, or radius of pit
T	= absolute temperature

Greek Letters

ν	= frequency of vibration

ρ = density on surface

ϵ = probability of abstraction of a carbon atom upon a collision by oxygen atom

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