

CARBON-CARBON DIOXIDE REACTION: LANGMUIR-HINSHELWOOD KINETICS AT INTERMEDIATE PRESSURES

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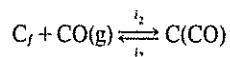
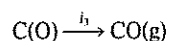
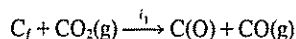
Abstract—The gasification of a very high purity natural graphite was studied at temperatures between 900 and 1007°C, at total gas pressures between 15 and 150 torr, and CO/CO₂ ratios between 0.098 and 2.0. Reactivity, expressed as weight loss per unit time, was constant over the burn-off range between about 10–50%. Rates of gasification were seen to obey the equation derived from Langmuir–Hinshelwood theory, that is $\text{Rate} = k_1 p_{\text{CO}_2} / (1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2})$. If it is assumed that the inhibition of gasification by CO is caused by its lowering the steady-state concentration of oxygen complex which breaks down to product CO, individual rate constants for the oxygen transfer and gasification steps can be calculated. Values of these rate constants and the equilibrium constant for the oxygen transfer step are considered in the light of literature results and theory.

1. INTRODUCTION

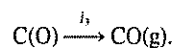
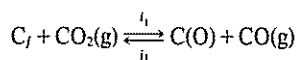
As has been popular in the broad field of gas–solid interactions, a number of attempts have been made to use the Langmuir–Hinshelwood theory to treat the kinetics of the C–CO₂ reaction [1–4], i.e. $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$. Walker *et al.* [5] showed that the Langmuir–Hinshelwood theory predicts an equation of the following form for the gasification of carbon by CO₂

$$\text{Rate} = \frac{k_1 p_{\text{CO}_2}}{1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2}} \quad (1)$$

whether CO inhibits the reaction by chemisorbing on active sites (mechanism A)



or by reducing the equilibrium concentration of oxygen complex on the carbon surface (mechanism B)



The above workers found that eqn (1) was successful in correlating their kinetics; but from a scientific viewpoint it is important to know whether their success is founded on a theoretical or, simply, on an empirical basis. Unfortunately, these workers used as carbons coconut shell charcoal, coal coke, anthracite and electrode carbon. These materials are complex solids poorly defined

crystallographically and containing significant amounts of metallic and/or hetero atom impurities. In some cases, questions arise as to the role which gas mass transport within the porous carbons played in affecting the measured rate constants [5]. Thus, the previous kinetic studies do not permit a decision to be made as to whether the successful use of the Langmuir–Hinshelwood approach means that the mechanism of the reaction has been uniquely deduced. In this study of the C–CO₂ reaction, a highly crystalline natural graphite of very high purity has been used. Further, mass transport resistance has been shown conclusively to be negligible. It is felt that a critical evaluation of the Langmuir–Hinshelwood kinetics can now be made.

2. EXPERIMENTAL

2.1 Graphite

The carbon employed in this study was SP-1 spectroscopically pure natural graphite from the Carbon Products Division of Union Carbide Corporation. It is supplied in the form of flakes about 0.3–0.5 μm in thickness and 30 μm in diameter [6]. It has a BET surface area of 1.8 m²/g and a He density of 2.25 g/cm³. From quantitative X-ray diffraction studies on the (0004) diffraction peak, using an internal standard [7], the interlayer spacing of the material was measured to be 3.3541 Å at 15°C. Based on the Franklin [8] and Bacon [9] correlation, this indicates that the material has a minimum of stacking faults between the layer planes. Particles were examined by direct transmission electron microscopy. As shown by Dawson and Follett [10, 11] when the long axis of the particle runs parallel to the (000 l) layer planes (as in the present case), crystallites in the particle are revealed by distinct and separate Moiré patterns produced by gross stacking faults within individual crystallites. As expected from X-ray diffraction studies, the appearance of Moiré patterns in SP-1 graphite is rare. Further, in most cases, there was no indication of the presence of micro-crystallites composing the particles. Selected area elec-

tron diffraction studies produced, in most cases, single crystal patterns. On the basis of these results, it is concluded that the particles are essentially non-porous. By taking the top and bottom faces of the flake-like particles as being composed of basal planes [(0001) surface] and the circumference of the particles as being composed of prismatic planes ($10\bar{1}0$ and $11\bar{2}0$ surfaces), $10\bar{1}0$ and $11\bar{2}0$ planes are estimated to account for approximately 3.3% of the total surface area of the particles.

Total impurity content of the graphite is guaranteed to be <1 ppm. The only impurities identified were: Si, Mg and Al.

2.2 Sample preparation

Artifacts were prepared by compacting SP-1 graphite powder at room temperature and a pressure of 100,000 psi. The samples produced had a BET surface area of $1.8 \text{ m}^2/\text{g}$, an apparent density of $2.18 \pm 0.03 \text{ g/cm}^3$, and a porosity of $4 \pm 2\%$. The compacted samples were milled into plates $3/8 \times 1$ in. by either $1/16$ or $1/32$ in. in thickness. A $1/8$ in. hole was drilled into one end of each plate so that it could be suspended on either a Pt or mullite hook. In this way, a minimum area of the sample came into contact with a foreign material. If loose SP-1 powder had been used, it would have been held in a boat, resulting in a significant increase in contact area. This was deemed undesirable because of our concern about graphite contamination and resulting catalysis of the gasification reaction[5].

Since purity of the sample was a prime consideration, the finished graphite plates were heat treated to 2500°C to remove impurities added during the compaction and milling process. From emission spectroscopy results, it was concluded that the final plates were as pure as the as-received graphite powder.

When the graphite plates were gasified in CO_2 , their rate of gasification per unit starting weight increased continuously with reaction time until a weight loss of about 10% was produced. Between about 10 and 50% weight loss, the gasification rate was constant. Presumably the available number of active sites did not change in this weight loss range[12]. Therefore, prior to our kinetic studies the plates were gasified to 10% weight loss at 1150°C in a flowing 10% CO -90% CO_2 gas stream at a total pressure of 1 atm. Carbon monoxide was added to make possible uniform gasification through the plates[13].

2.3 Gases

Gases were obtained from the Matheson Company. The CO_2 was "Coleman grade", having a minimum purity of 99.99 vol %. The CO was "C.P. grade", having a minimum purity of 99.5 vol %. The gases were passed through 13X molecular sieves to remove water and then over hot Cu turnings at 550°C to remove oxygen. By mass spectrometric analyses no O_2 , H_2 or H_2O was found in either CO or CO_2 (meaning the presence of <0.01%).

2.4 Apparatus

The apparatus consisted of the following sections: gas purification, gas storage, gas dosing and reactor. It has

been described in detail elsewhere[14]. Briefly, the weight decrease of the graphite during gasification by CO_2 was followed using a quartz beam microbalance of the type described by Rhodin[15]. The balance housing, which was fashioned of 65 mm diameter Pyrex tubing, was connected to twin clear fused quartz tubes 34 mm i.d. Into one tube was hung a counter weight; into the other tube, was hung the graphite plate by a 0.007 in Pt-Ir wire. A Gaertner slide micrometer microscope was used to follow movement of the balance beam; weight losses down to 10^{-6} g could be accurately measured.

To minimize permeation of external gases at high temperatures in the reaction space, the hang-down tubes were constructed with a double wall, with the annular space between the walls being continuously outgassed. Using a two-stage Hg diffusion pump, a vacuum of 10^{-6} torr could be attained in the reaction space at 1000°C .

The reactor temperature was controlled within $\pm 2^\circ\text{C}$ between reaction temperatures of 902 - 1007°C by a Series 60 Leeds and Northrup unit. The furnace had a constant temperature zone of about 3 in. in length, in which the sample was located.

The remainder of the system was a standard Pyrex glass high vacuum apparatus, using ground glass stopcocks. Five separate pressure indicators (Pirani gage, thermocouple gage, Zimmerli gage, Hg manometer and McLeod gage) permitted adequate pressure measurements to be made between 10^{-6} and 200 torr.

2.5 Reactivity runs

Procedures employed in obtaining reactivity data are described in detail elsewhere[14]. With the graphite sample in place in the reactor, the apparatus was outgassed and the walls "flamed out" until a vacuum of 10^{-5} torr was attained. The reactor was then brought to the desired temperature; the sample was soaked for 3 hr after a vacuum of 10^{-6} torr was attained and before reactivity runs were started. Following admission of the desired CO - CO_2 mixture into the reactor, about 5 min were required for the balance to settle down sufficiently so that accurate readings of deflection could be taken. This was selected as zero reaction time. The maximum weight loss necessary to obtain an accurate reactivity measurement was about 0.03% or 100 μg . Since reactivity was constant between about 10-50% weight loss, all kinetic data could be obtained on one sample if desired. This is a distinct advantage.

Runs were made at total gas pressures between 10 and 150 torr. At higher pressures, gas convective currents disturbed the balance unduly. Over the reaction temperature range used, 902 - 1007°C , the duration of typical runs varied from 12 hr to 25 min.

If eqn (1) is inverted, it can be written as

$$\frac{1}{\text{Rate}} = \frac{k_3}{k_1} + \frac{k_2}{k_1} \frac{p_{\text{CO}}}{p_{\text{CO}_2}} + \frac{1}{k_1} \frac{1}{p_{\text{CO}_2}} \quad (2)$$

In principle, the rate constants in eqn (2) can be determined from reactivity results obtained when: (i) $p_{\text{CO}}/p_{\text{CO}_2}$ is held constant and the total pressure varied, (ii) p_{CO_2} is held constant and p_{CO} varied and (iii) p_{CO} is held

constant and p_{CO_2} varied. Use of the first method proved the most suitable. A reactivity run was made in a gas mixture of predetermined p_{CO}/p_{CO_2} ratio at the lowest total pressure. A series of subsequent runs were made up to the highest total pressure by adding fresh aliquots of gas of the same p_{CO}/p_{CO_2} ratio. There was no outgassing between runs. Each reactivity run was constant from zero reaction time. After a set of reactivity runs at one p_{CO}/p_{CO_2} ratio and one temperature was completed, the system was outgassed to 10^{-6} torr and held for 3 hr prior to making runs at a new p_{CO}/p_{CO_2} ratio. Before going to a new temperature, the system was outgassed at 10^{-6} torr for 12 hr; the system was then outgassed an additional 3 hr at the new gasification temperature.

In practice, the second method of obtaining rate constants was possible but not the most convenient. Using this method, the first run was made with a 10% CO-90% CO_2 mixture ($p_{CO}/p_{CO_2} = 0.111$). Subsequent runs at the same temperature were made following the addition of aliquots of pure CO. For those subsequent runs, the time required for the sample reactivity to equilibrate to a new value was long.

To use the third method to obtain kinetic data, $p_{CO_2}/rate$ is plotted vs p_{CO_2} , and rate constants are calculated from the slope and intercept. In this investigation, this method was not practical, however, since the slopes of the plots were very close to zero; and the experimental precision did not permit accurate evaluations of very small differences in slope from zero. A slope close to zero means that the graphite gasification rate was close to first order in p_{CO_2} at constant p_{CO} .

During gasification, p_{CO} progressively increased and p_{CO_2} progressively decreased. However, since the system volume in which the gas mixture was held was large (2250 cm^3) and the amounts of carbon gasified were very small, the maximum change in the p_{CO}/p_{CO_2} ratio produced was <2%. Such changes had a negligible effect on gasification rates for the range of p_{CO}/p_{CO_2} ratios used in this study.

Since a large number of runs were made on one sample, we were concerned about the previous history of the sample affecting our results. Consequently, we selected as a standard condition 50 torr of 10% CO-90% CO_2 at 977°C. Frequently during the course of this study, samples were returned to this condition and their reactivity measured. Gasification rates in all cases agreed within $\pm 3\%$. Outgassing times at reaction temperature between 3 and 72 hr had no detectable effect on rates. The sequence of reaction temperatures used was deliberately randomized to avoid any trend in the nature of active sites developed [16]. Whether the graphite sample was suspended on a Pt or mullite hook showed no effect.

3. RESULTS

3.1 Rates for constant CO/ CO_2 ratios

Graphs obtained by plotting reciprocals of observed rates vs reciprocals of CO_2 pressures, when the CO/ CO_2 ratio is held constant, yielded good straight lines as expected from eqn (2). Figure 1 presents results for runs at 952°C and at three different CO/ CO_2 ratios. The units of rate are g carbon reacting per hour per g of starting carbon

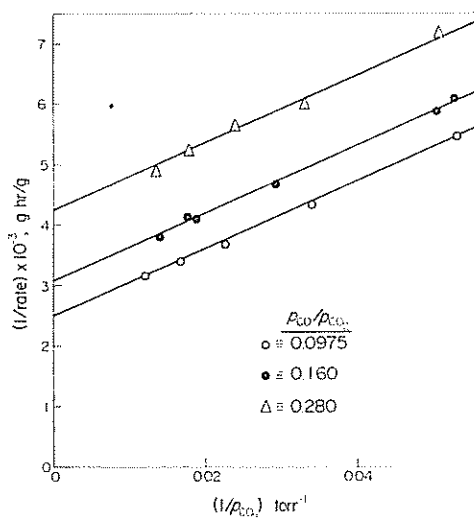


Fig. 1. Test of eqn (2) for constant p_{CO}/p_{CO_2} ratios at 952°C and p_{CO_2} pressures ranging from 19 to 80 torr.

weight. As would be expected from eqn (2), the lines are parallel and differ only in their intercepts. This is a consequence of the slope of the plots being equal to k_1^{-1} . From plots such as these, rate constants k_1 , k_2 and k_3 were calculated.

Table 1 presents a compilation of all the data that were obtained at constant CO/ CO_2 ratios. The pressure limits within which all data were obtained extended from 19 to 120 torr, and the temperature limits extended from 902 to 1007°C. Over 100 individual rate determinations were made in order to evaluate the constants. Where only one CO/ CO_2 ratio is reported, the constants k_2 and k_3 were

Table 1. Results obtained by varying p_{CO_2} at constant p_{CO}/p_{CO_2} ratios

Temp. (°C)	$\frac{p_{CO}}{p_{CO_2}}$	Experimental data			Least squares values		
		$k_1 \times 10^4$	$\frac{k_2}{10^5}$	$\frac{k_3}{10^5}$	$k_1 \times 10^4$	$\frac{k_2}{10^5}$	$\frac{k_3}{10^5}$
1007	0.0975	20.5	119	25.6	21.1	120	25.4
982	0.160	10.2	135	22.5	10.1	132	23.0
982	0.280	10.1	130	23.5	10.1	132	23.0
977	0.0975	7.80	129	23.0	8.18	135	22.6
952	0.0975	3.61	151	20.0	3.64	151	20.4
952	0.0975	3.72	154	20.4	3.64	151	20.4
952	0.0975	3.69	146	21.0	3.64	151	20.4
952	0.0975	3.61	152	20.0	3.64	151	20.4
952	0.160	3.72	148	22.0	3.64	151	20.4
952	0.280	3.69	150	21.0	3.64	151	20.4
950	0.0975	3.20	156	20.6	3.47	153	20.2
937	0.0975	2.27	171	19.0	2.33	162	19.2
932	0.105	1.83	169	18.6	1.82	166	18.8
932	0.243	1.84	168	18.7	1.82	166	18.8
932	0.375	1.83	170	18.6	1.82	166	18.8
932	0.375	1.82	168	18.6	1.82	166	18.8
922	0.160	1.39	174	18.1	1.38	172	18.1
922	0.280	1.39	174	18.1	1.38	172	18.1
902	0.105	0.65	192	16.6	0.65	192	16.6
902	0.243	0.66	189	16.5	0.65	192	16.6

Units of: $k_1 = (\text{g of carbon reacting} \times \text{cm}^3 \text{ of } CO_2) / (\text{g of initial carbon weight} \times \text{sec} \times \text{moles of } CO_2)$;

$k_2 = (\text{cm}^3 \text{ of } CO / \text{mole of } CO)$;

$k_3 = (\text{cm}^3 \text{ of } CO_2 / \text{mole of } CO_2)$.

evaluated either by varying the CO pressure at constant CO₂ pressure, as was done in most cases, or by using a single reaction rate at a different CO/CO₂ ratio, as was done in two cases. Table 1 has two columns for each rate constant, i.e. the experimental data and the corresponding values obtained from least squares Arrhenius plots.

3.2 Rates for varying CO/CO₂ ratios

Below a CO/CO₂ ratio of about 2, results obtained by varying the CO/CO₂ ratio, while the CO₂ pressure was being held constant, gave quite acceptable results. Graphs obtained by plotting reciprocals of observed rates vs CO/CO₂ ratios yielded good straight lines as expected from eqn (2). Figure 2 shows such a plot for results taken at 1007°C and a p_{CO_2} of 20 torr. Table 2 summarizes results obtained. The constants k_2 and k_3 were evaluated, using k_1 values previously obtained at constant CO/CO₂ ratios.

3.3 Compilation of rate constant values

The rate constants obtained from both of the above methods are placed on Arrhenius plots in Figs. 3 and 4 and least square lines drawn through all the points. Scatter is least on the Arrhenius plot for k_1 ; scatter on the k_2 and k_3 plots is comparable. Note that results in Fig. 3 are independent of whether a 1/32 or 1/16 in. thick sample was used, i.e. rates were not affected by resistance to mass transport.

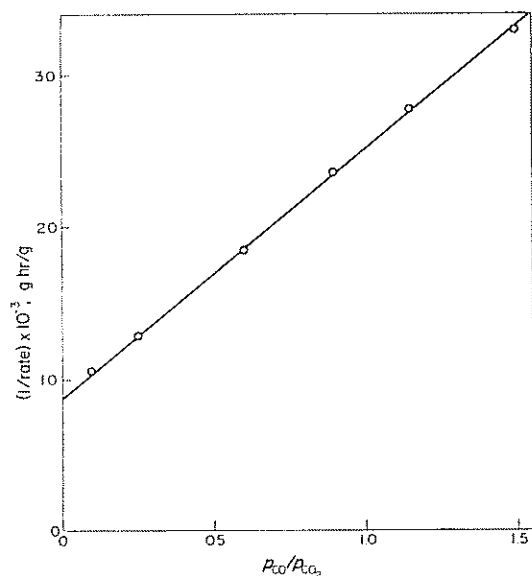


Fig. 2. Test of eqn (2) for constant $p_{CO_2} = 20$ torr at 1007°C and changing p_{CO}/p_{CO_2} ratio.

Table 2. Results obtained by varying p_{CO}/p_{CO_2} at constant p_{CO_2}

Temp. (°C)	p_{CO_2} (torr)	$(k_2/k_1) \times 10^{-4}$	$k_1 \times 10^1$	$k_2 \times 10^{-5}$	$k_3 \times 10^{-5}$
1007	20.0	5.8	20.7	120	25.4
967	20.5	25.7	5.64	143	21.7
952	24.2	41.3	3.70	154	20.4
952	34.5	39.6	3.70	146	21.0
952	41.6	42.1	3.62	152	20.0
937	19.5	68.0	2.42	164	19.2
917	21.0	178.0	1.02	180	17.8

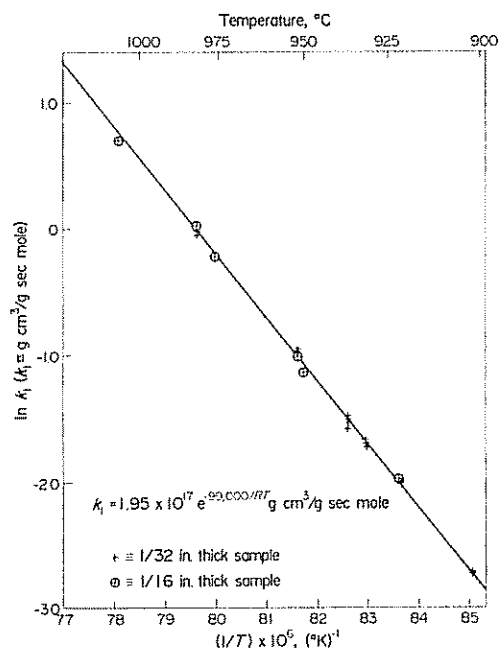


Fig. 3. Arrhenius plot of k_1 for graphite plates of 1/32 and 1/16 in. thicknesses.

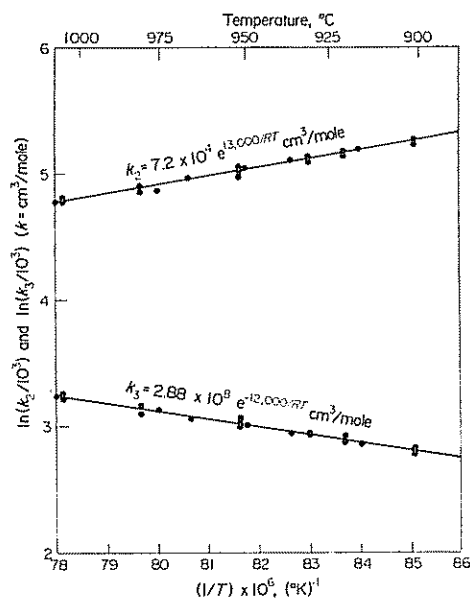


Fig. 4. Arrhenius plots of k_2 and k_3 for graphite plates of 1/32 and 1/16 in. thicknesses.

It would be more useful if k_1 was expressed on the basis of active sites instead of on a carbon weight basis. From studies on the chemisorption of oxygen on SP-1 graphite, Walker *et al.*[6] concluded that 15.6 μg of active sites were present for each gram of carbon. On the basis of this active site value, $k_1 = 1.25 \times 10^{22} \exp(-99,000/RT)$ g carbon cm^3/g active sites sec mole CO₂. It would be interesting to see if this value would be able to adequately describe the reactivity of other high purity carbons for which the number of active sites is known.

If mechanism B is accepted to describe the C-CO₂ reaction, as suggested by Ergun[17], the rate constants k_1 ,

k_2 and k_3 in turn are given by[5]: $k_1 = i_1$, $k_2 = j_1/j_3$ and $k_3 = i_1/j_3$. Values for i_1 , j_1 and j_3 are given in Table 3.

4. DISCUSSION

4.1 Thermochemical considerations

On the basis of mechanism B it is possible to use the energies obtained for k_1 , k_2 and k_3 to illustrate how the various energies and heats are involved in the C-CO₂ reaction. From Fig. 5, it is seen that from this work the heat of reaction for the first step of the C-CO₂ reaction, the oxygen exchange reaction, was found to be 25 kcal/mole endothermic. This heat compares favorably with the value of 23 kcal/mole reported previously by Ergun[17]; however, the line gives values of K_{eq} which fall somewhat below Ergun's values. Values of K_{eq} , as given by Tonge[18], are also shown on Fig. 5.

Thermochemical calculations can be made in order to ascertain whether the heat found for the oxygen exchange reaction is reasonable. One difficulty in making precise calculations lies in uncertainty concerning the nature of the carbon-oxygen bond in the complex. Walker *et al.*[6], who used thermoelectric power measurements to follow the kinetics of oxygen chemisorption onto SP-1 graphite from O₂, have shown that formation of the oxygen complex involves some localization of a π -electron from the graphite. This localization results in some loss of

carbon-carbon bond energy within the graphite. Taking reasonable values for the strengths of carbon-carbon and carbon-oxygen single and double bonds, Strange showed that if the carbon-oxygen bond in the oxygen complex has two-thirds double bond character, good agreement is found between the heat calculated for the oxygen transfer reaction [C₁ + CO₂(g) → CO(g) + C(O)] and the value found experimentally in this paper, that is 25 kcal/mole[14].

4.2 Kinetic considerations

Values found experimentally for the rate constants for the formation of oxygen complex and its breakdown to give CO can be considered as to whether they appear reasonable. Consider first the rate constant j_3 for the breakdown on desorption of the oxygen complex. According to absolute rate theory[19], the pre-exponential factor is given by

$$A = \frac{k_B T f^*}{h f_a}$$

where k_B is the Boltzmann constant; T , the absolute temperature; h , Planck's constant; and f^* and f_a the partition functions of the transition state complex and the adsorbed species C(O), respectively. If as was found by Blyholder and Eyring for the breakdown of the complex in the C-O₂ reaction, the ratio of f^*/f_a is equal to one, A at 954°C (mean temperature in this study) has a value of $2.6 \times 10^{13} \text{ sec}^{-1}$. This value compares favorably with the experimental value of $4.4 \times 10^{13} \text{ sec}^{-1}$.

The activation energy associated with the breakdown of the oxygen complex is 87 kcal/mole. This value may be compared to the energy required to split a carbon-carbon bond. A number of workers[20, 21] have found that the dissociation energies of various carbon-carbon bonds range from 72 to 83 kcal/mole. Unfortunately, no values were found in the literature for splitting CO from bonds similar to those which exist in this study, i.e. from quinone or phenanthrenequinone. In other studies, activation energies ranging from 70 to 90 kcal/mole were reported by Wicke[22], Armington[23], Meyer[24] and Turkdogan and Vinters[25]. Blyholder and Eyring[26], who studied the C-O₂ reaction, report an activation energy of 80 kcal/mole for the breakdown of the C(O) surface complex to give CO(g). In contrast, Ergun reported an activation energy value of 59 kcal/mole for the product $j_3(C_1)$ in the C-CO₂ reaction, where C_1 is the total number of active sites[17]. Assuming that C_1 did not change with temperature, Ergun attributed the activation energy to j_3 .

Consider now the rate constant i_1 , the forward step in the oxygen exchange reaction. The activation energy of 99 kcal/mole exceeds values previously reported [1-3, 27] on coconut shell charcoal (58.8), coal coke (47.9 and 61.7), electrode carbon (50.1) and nuclear graphite (71 kcal/mole). However, these carbons are more or less impure; and, therefore, dissociation of the CO₂ could have been occurring primarily over metal or metal oxide sites. According to Rossberg and Wicke[28], the energy required to effect the transfer of an oxygen atom from CO₂ to the carbon in the C-CO₂ reaction should be close

Table 3. Derived rate constants for mechanism B

Rate constant	Value
i_1	$1.25 \times 10^{22} \exp(-99,000/RT) \text{ cm}^3/\text{mole sec}$
j_1	$3.14 \times 10^{16} \exp(-74,000/RT) \text{ cm}^3/\text{mole sec}$
j_3	$4.35 \times 10^{13} \exp(-87,000/RT) \text{ sec}^{-1}$

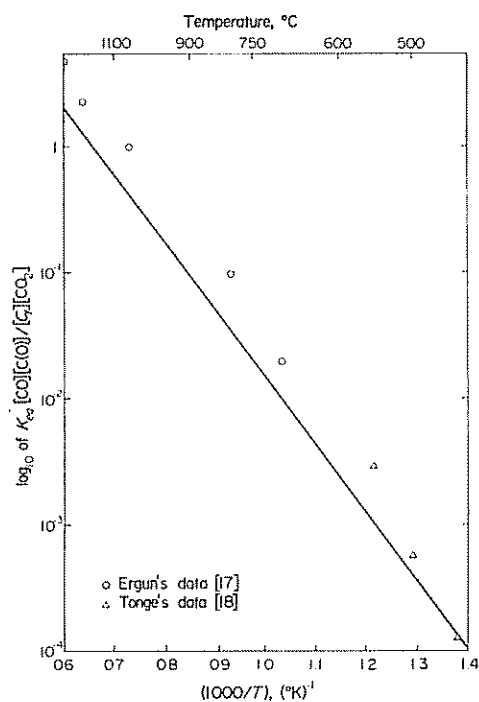


Fig. 5. Equilibrium constant for the oxygen exchange reaction as a function of temperature. $K_{eq} = 4.0 \times 10^3 \exp(-25,000/RT)$.

to the energy required to remove the first O atom from CO₂. The dissociation energy of this bond is 127 kcal/mole [29].

The pre-exponential term in i_1 can be compared with the maximum possible value as predicted by collision theory, in the simplest case. The number of collisions of reacting molecules with the surface per unit time is estimated from the kinetic theory of gases as $N\bar{c}/4$, where N is the gas concentration and \bar{c} is the average velocity of the molecules. At 952°C and 1 atm CO₂ pressure, the frequency of collisions is calculated to be 1.2×10^{23} molecules/cm² sec. In order to compare the frequency of collisions of CO₂ molecules with the surface with the pre-exponential factor in i_1 , the pre-exponential factor is multiplied by the concentration of CO₂ at 1 atm and 952°C (i.e. 9.9×10^{-6} mole/cm³) and divided by the area occupied by an active site on the carbon surface (i.e. about 8.3×10^{-16} cm²). Thus the pre-exponential factor is converted from 1.25×10^{22} cm³/mole sec to 1.5×10^{32} molecules/cm² sec. Obviously this factor should not be larger than the frequency of collisions of CO₂ with the surface. To the extent that all molecules colliding with the active sites on the surface do not have the proper orientation for reaction (i.e. the steric factor is <1), the pre-exponential factor should be less than the frequency of molecules colliding with the active sites. Indeed, this was found to be the case, in studies in this laboratory on the C-O₂ reaction [12].

It has recently been suggested [30] that the entire basal plane of carbon may serve as a "collector area" for the reacting molecules, even though reaction does not occur on the basal surface but just at its edge (active sites). That is, molecules collected on the basal plane diffuse across it to the edge where reaction occurs. In this case the area assigned to an active site on the surface of the SP-1 graphite would obviously have to be increased. Walker *et al.* [6] have shown that the edge area of SP-1 graphite constitutes about 3.3% of the total surface. Thus the "effective area" assigned to an active site in SP-1 graphite, assuming that all of the basal plane area is acting as collector area, would be about 30 times greater than the value of 8.3×10^{-16} cm² taken originally. This would decrease the pre-exponential factor in i_1 to 5×10^{30} molecules/cm² sec, which is still much greater than the value for frequency of collisions of CO₂ with the surface.

A number of authors have discussed possible reasons for the compensation effect, i.e. when the activation energy goes up the pre-exponential factor also goes up [31, 32]. As noted earlier the activation energy for i_1 is large. This, in turn, results in the pre-exponential factor for i_1 being large. However, as we will see in the next paper [33], the activation energy for i_1 for the gasification of SP-1 graphite by CO₂ at very low pressures is, indeed, large and agrees well with the value found in this study. Obviously, it brings into question just what an activation energy means, in a fundamental way, for the steps in carbon gasification.

In any case as will be discussed in the next paper [33], if

sample outgassing prior to gasification is conducted under more extreme conditions than used in this study, that is 10^{-8} torr and 1100°C, gasification rates are increased. Thus there is clearly no one set of rate constants for the C-CO₂ reaction.

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REFERENCES

- Gadsby J., Long F. J., Sleightholm P. and Sykes K. W., *Proc. Roy. Soc. (London)* A **193**, 357 (1948).
- Lewis W. K., Gilliland E. R. and McBride G. T., Jr., *Ind. Engng Chem.* **41**, 1213 (1949).
- Wu P. C., D. Sci. Thesis, Massachusetts Institute of Technology (1949).
- Reif A. E., *J. Phys. Chem.* **56**, 778 (1952).
- Walker P. L., Jr., Rusinko F., Jr. and Austin L. G., *Advances in Catalysis*, Vol. 11, p. 133. Academic Press, New York (1959).
- Walker P. L., Jr., Austin L. G. and Tietjen J. J., *Chemistry and Physics of Carbon*, Vol. 1, pp. 327-365. Marcel Dekker, New York (1965).
- Walker P. L., Jr., McKinstry H. A. and Pustinger J. V., *Ind. Engng Chem.* **46**, 1651 (1954).
- Franklin R. E., *Acta Cryst.* **4**, 253 (1951).
- Bacon G. E., *Acta Cryst.* **4**, 558 (1951).
- Dawson I. M. and Follett E. A. C., *Proc. Roy. Soc. (London)* **A253**, 390 (1959).
- Dawson I. M. and Follett E. A. C., *Proc. Roy. Soc. (London)* **A274**, 386 (1963).
- Laine N. R., Vastola F. J. and Walker P. L., Jr., *J. Phys. Chem.* **67**, 2030 (1963).
- Austin L. G. and Walker P. L., Jr., *A.I.Ch.E. J.* **9**, 303 (1963).
- Strange J. F., Ph.D. Thesis, Pennsylvania State University (1964).
- Rhodin T., *Advances in Catalysis*, Vol. 5, p. 39. Academic Press, New York (1953).
- Thomas J. M., *Chemistry and Physics of Carbon*, Vol. 1, pp. 121-202. Marcel Dekker, New York (1965).
- Ergun S., *J. Phys. Chem.* **60**, 480 (1956).
- Tonge B. L., *Proc. Fourth Carbon Conf.*, p. 87. Pergamon Press, New York (1960).
- Glasstone J., Laidler K. J. and Eyring H., *The Theory of Rate Processes*. McGraw-Hill, New York (1941).
- Adams G. K. and Bawn C. E. H., *Trans. Faraday Soc.* **45**, 494 (1949).
- Andersen H. C., Kistiakowski G. B. and van Artsdalen E. R., *J. Chem. Phys.* **10**, 305 (1942).
- Wicke E., *Fifth Symposium on Combustion*, p. 245. Reinhold, New York (1955).
- Armington A. F., Ph.D. Thesis, The Pennsylvania State University (1961).
- Meyer L., *Trans. Faraday Soc.* **34**, 1056 (1938).
- Turkdogan E. T. and Vinters J. V., *Carbon* **7**, 101 (1969).
- Blyholder G. and Eyring H., *J. Phys. Chem.* **61**, 682 (1957).
- Hedden K. and Lowe A., *Carbon* **5**, 339 (1967).
- Rossberg M. and Wicke E., *Chemie Ing. Techn.* **28**, 181 (1956).
- Cottrell T. L., *The Strength of Chemical Bonds*. Butterworths, London (1958).
- Feates F. S. and Robinson P. S., *Third Conf. on Industrial Carbon and Graphite*, p. 233. Society of Chemical Industry, London (1971).
- Cremer E., *Advances in Catalysis*, Vol. 7, p. 75. Academic Press, New York (1955).
- Bond G. H., *Catalysis by Metals*, p. 139. Academic Press, New York (1962).
- Biederman D. L., Miles A. J., Vastola F. J. and Walker P. L., Jr., **14**, 351 (1976).