

THE INFLUENCE OF "INERT" DILUENT GASES ON THE RATE OF CARBON GASIFICATION

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(Received 10 August 1976)

Abstract—The effect of diluent gases on gasification rates of the C-O₂ and C-CO₂ reactions has been studied. At equal starting pressures of reactant and diluent, rates for both reactions are: N₂ > Ar > He. For the C-CO₂ reaction, the presence of a diluent results in higher gasification rates than when no diluent is present in the order: Xe > N₂ > Ar. Possible reasons for the diluent effects are discussed.

1. INTRODUCTION

Recently it has been noted that the rates of some heterogeneous catalytic reactions are affected by the presence of different "inert" diluent gases [1-3]. The most prominent example is the catalytic oxidation of SO₂ over a vanadia catalyst. Also the rates of solid state reactions and phase transformations are reported to be affected [1]. Explanations for the effects include: (i) enhanced rates of desorption of product species as a result of collision of diluent molecules with them, (ii) differences in the efficiency of removal or input of heat upon collision of diluent molecules with active sites, (iii) changes in the mobility of reactant and/or product species on the surfaces and (iv) van der Waals adsorption of diluent at an activated complex in the reaction and thereby affecting the bonding between the activated complex and the surface.

In the case of carbon gasification, no "inert" diluent gas effects on rates have been reported, to the authors' knowledge, that could not be ascribed to rate retardation because of increased resistance to diffusion of reactant to the carbon surface. In this study, possible effects of diluent on the rates of the C-O₂ and C-CO₂ reactions have been examined under conditions where diffusional limitations in the gas phase were not a significant factor.

2. EXPERIMENTAL

2.1 Apparatus

2.1.1 C-O₂ reaction. The apparatus used to measure rates of the C-O₂ reaction consisted of the following sections: gas purification, gas storage, gas dosing and reactor. Weight decrease of the carbon during gasification was followed using a quartz beam microbalance of the type designed by Gulbransen [4]. It had a sensitivity of 10⁻⁶ g. The apparatus is described in detail elsewhere [5]. Briefly, the microbalance housing was made of Pyrex, with the balance itself resting on a quartz block accessible through a 55/50 ground glass joint. The horizontal balance housing was connected to the vertical reactor tube and a counterweight tube through two water cooled joints. Removal of these joints permitted the addition of the sample and counterweight. The reactor proper was a mullite tube.

The carbon sample was held in a quartz boat suspended

from the balance by a platinum wire. The system was evacuated through a mechanical pump and an oil diffusion pump. Prior to reaction, the sample was outgassed at 950°C to a vacuum of 10⁻⁵ torr for 90 min.

2.1.2 C-CO₂ reaction. To follow the rate of the C-CO₂ reaction at low pressures the rates of disappearance of CO₂ and appearance of CO were followed using a CEC Type 26-611 mass spectrometer as described previously [6]. Molded graphite plates were suspended from a mullite rod in the vertical quartz reactor tube. The reactor system (11.6l) was connected directly to the inlet leak of the mass spectrometer analyzer tube. Because of the large reactor volume, the amount of gas removed at intervals for analysis had an insignificant effect on the total pressure in the reactor.

The reactor tube was surrounded with a quartz jacket. The space between the reactor and jacket was kept evacuated to a pressure of <0.25 mtorr. Prior to reaction, samples were outgassed at 1130°C for 12 hr, using an oil diffusion pump, to a vacuum better than 10⁻⁷ torr.

2.2 Materials used

2.2.1 Carbons. For the C-O₂ studies, a P-33 gas thermal black obtained from Cabot Company was used. It was heat treated at 2700°C for 2 hr. It had the following properties: BET surface area, 12 m²/g; particle diameter, 2000 Å; *c*-spacing, 6.80 Å; \bar{L}_c , 140 Å and \bar{L}_a , 125 Å.

For the C-CO₂ studies, SP-1 spectroscopically pure natural graphite from the Carbon Products Division of Union Carbide was used. It was supplied in the form of flakes about 0.3-0.5 μm in thickness and 30 μm in diameter [7]. It had a BET surface area of 1.8 m²/g, a He density of 2.25 g/cm³, and a *c*-spacing of 6.7082 Å. This graphite was highly crystalline, with excellent crystallite alignment within the particle. Total impurity content of the graphite was <1 ppm. Artifacts were prepared by compacting the graphite at room temperature and 100,000 psi into plates 1/16 and 1/8 in. in thickness. The graphite plates were heat treated to 2500°C to remove impurities possibly added during compaction.

When the graphite plates were gasified with CO₂, their rate of gasification per unit starting weight increased continuously with reaction time until a weight loss of about 10% was produced. Between 10 and 50% weight

loss, the gasification rate was constant. Therefore, prior to kinetic studies the plates were gasified to 10% weight loss at 1150°C in a flowing 10%CO-90%CO₂ atmosphere at a total pressure of 1 atm. Carbon monoxide was added to make possible uniform gasification through the plates[8]. Unlike the C-O₂ reactivity studies where a new sample of carbon was used for each run, for the C-CO₂ reaction one carbon sample was used for all runs, with burn-off for each run being <0.1%.

2.2.2 *Gases.* All gases were obtained from the Matheson Company. They had the following minimum purity: O₂, 99.6%; N₂, 99.7%; He, 99.99%; Ar, 99.998%; CO₂, 99.99% and Xe, 99.995%.

3. RESULTS

3.1. C-O₂ reaction

All reaction rate determinations were carried out at 0.1 atm total gas pressure and reaction temperatures between 550 and 616°C up to burn-offs of about 4%. Using a fixed outgassing procedure, duplicability of gasification rates, expressed as weight gasified per unit time per unit starting weight, was within ±2% in all cases. Burn-off plots were independent of sample weight, between 0.0250 and 0.0500 g, indicating that diffusional resistance of reactants and products through the porous carbon bed had a negligible effect on reactivity. The activation energy for reaction calculated from Arrhenius plots was 55 ± 2 kcal/mole over the burn-off range 1-4%.

While maintaining the total pressure at 0.1 atm, the partial pressure of O₂ was varied from 0.075 to 0.025 atm by the addition of N₂, Ar or He. Figure 1 presents gasification runs at 616°C. In every case the rates, in

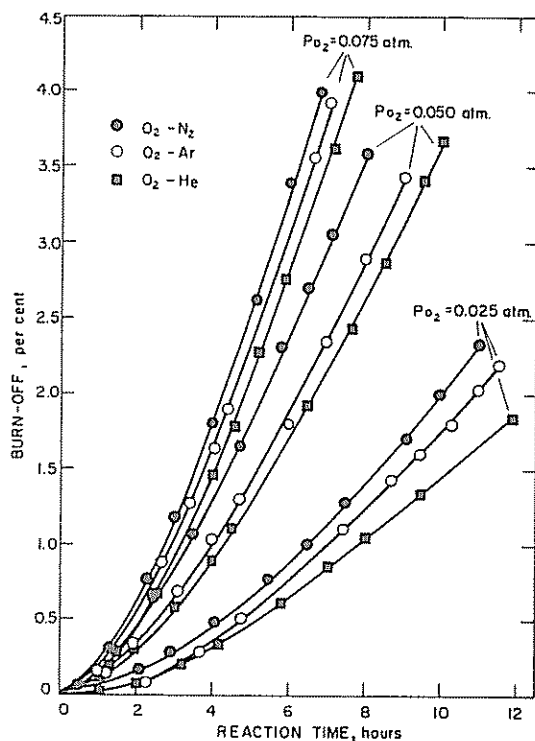


Fig. 1. Reaction rate curves at 616°C and 0.1 atm total pressure for different partial pressures of O₂ and different diluents.

decreasing order, are: O₂-N₂, O₂-Ar and O₂-He. Similar results were found at 598°C.

3.2. C-CO₂ Reaction

The reaction was conducted at 1100°C with starting partial pressures of CO₂ and diluent of 50 mtorr each. Thus the total starting pressure was 100 mtorr in all cases, except when no diluent was added. At this low pressure the rate of the C-CO₂ reaction, which is normally given by the expression[9]:

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

is found to simplify to

$$\text{Rate} = k_1 p_{\text{CO}_2} \quad (2)$$

That is $k_2 p_{\text{CO}} + k_3 p_{\text{CO}}$ are small compared to one. Thus plots of $\log p_{\text{CO}_2}$ vs time gave straight lines for consumption of p_{CO_2} up to at least 80%, with the slope of the line equal to $-2.3k_1$. As described recently[10], duplicability of k_1 from run to run is only fair because of the strong inhibiting effects of traces of H₂, which may be in the reacting gas and/or on the reactor walls. Gasification rates were independent of whether plates 1/8 or 1/16 in. in thickness were used, indicating that diffusional resistance had a negligible effect on reactivity.

Table 1 summarizes reactivity results for all runs made. Without doubt, the presence of the diluents N₂ and Xe significantly increases the rate of the C-CO₂ reaction. Probably Ar also increases the reaction rate, with the effect of He being questionable. Particularly striking is Xe which approximately doubles the gasification rate.

4. DISCUSSION

In the course of these studies on the C-O₂ reaction in 1959, concerned with reaction orders, the diluent effect on gasification rates was first discovered. The effect was unexpected and in the absence of an explanation was not reported in the open literature. This was followed by additional studies of the diluent effect in 1965. In this second study we altered a number of conditions to see if the same diluent effects were found. In the 1959 and 1965 experiments the following were different: (i) the C-O₂ vs the C-CO₂ reaction, (ii) measurement of gasification rate by weighing vs gas analysis, (iii) a graphitized carbon black of relatively small crystallite size vs a large crystallite size natural graphite, (iv) a total pressure of 76 torr vs 100 mtorr and (v) a maximum temperature of 616°C vs 1100°C. For both experiments, there was an effect of diluent on gasification rates; and in both experiments the effect was qualitatively the same. That is, reactant-N₂ showed the greatest rate, reactant-Ar was intermediate in rate and reactant-He showed the lowest rate.

Some of the possible reasons for this diluent effect can be considered and some possibilities can clearly be eliminated. One possibility is the presence of critical impurities of varying amounts in the diluent gases. The two critical impurities which come to mind are O₂ and H₂.

Table 1. Summary of k_1 values for C-CO₂ reaction at 1100°C

Gas	Runs Made	k_1 , g cc/g sec mole
CO ₂	5	567 ± 143
CO ₂ -He	1	667
CO ₂ -Ar	1	787
CO ₂ -N ₂	2	932 ± 115
CO ₂ -Xe	2	1300 ± 103

Since the C-O₂ reaction is much more rapid than the C-CO₂ reaction[9], trace amounts of O₂ in the diluent gases for the C-CO₂ reaction could affect this reaction rate. However, this could not explain the diluent effect for the C-O₂ reaction. Hydrogen has been shown to markedly inhibit the C-CO₂ reaction[10], and trace amounts in the diluent gases could have variable effects. But addition of diluents did not decrease gasification rates; rather it increased rates. Therefore, explanations other than impurity effects are needed.

Mass transport effects in the gas phase can be eliminated. That is, the addition of an inert in the C-CO₂ studies doubled the pressure; thus it would have increased diffusional resistance. However, diluent addition increased the gasification rate. It would seem that mass transport effects on the carbon surface can also be eliminated. That is, gasification in part can be occurring by the dissociation of the reactant at impurity sites followed by the diffusion of an oxygen atom across the surface to an active carbon site where gasification occurs. At particular conditions of temperature and pressure, more diluent Xe (critical temperature, 16.6°C) than He (critical temperature, -268°C) will be adsorbed on the carbon surface. Thus Xe would be expected to decrease the rate of surface diffusion of oxygen atoms to a greater extent than would He. However, the gasification rate in CO₂-Xe is clearly greater than in CO₂-He.

Collisions between the intermediate oxygen surface complex and diluent may lead to an enhanced rate of removal of the complex as CO or CO₂ (that is gasification). Desorption of the complex is assumed to occur if the translational energy transfer from the diluent molecule to the surface complex during the collision exceeds the activation energy for desorption. This was the explanation originally put forth by Baron *et al.*[11] to explain their findings that the oxidation of SO₂ over a V₂O₅ surface to produce SO₃ was enhanced by the presence of a diluent. Goodman, however, carefully considered this possibility on a theoretical basis and concluded that the enhancement of thermal desorption by collision desorption would be negligible in all cases he could conceive of [2].

One might invoke a microscopic heat transfer argument. That is, for example, the C-O₂ reaction is exothermic; and, therefore, following gasification the new carbon surface site can be considered a "thermal spike". Its effective temperature is greater than that of the mean temperature of the solid (carbon). Heat removal from this site would occur via both conduction in the solid and

collisions with molecules from the gas phase. Assuming an infinite heat sink in the gas phase and a particular temperature and pressure, the rate at which heat would be transferred away from a "thermal spike" would be essentially proportional to the product of the number of collisions with the site per unit time and the accommodation coefficient of the gas molecule. The more rapidly the "thermal spike" cools down to the mean temperature, the lower the probability that collision with O₂ will lead to a new gasification event. At a particular temperature and pressure, the number of collisions with a site per unit time is proportional to the mean molecular velocity of the gas. The velocity for He is roughly three times that of N₂ or Ar. Unfortunately, accommodation coefficient data for these gases on carbon surfaces at gasification temperatures appear to be lacking. In any event, the "thermal spike" argument cannot explain the diluent effects, if one considers that the effect was the same for the C-O₂ and C-CO₂ reaction. That is, the C-CO₂ reaction is endothermic and a gasification event would leave the new surface carbon site at a temperature lower than the mean temperature. In this case, the more rapidly the site again attained the mean temperature the greater the probability that collision with CO₂ would lead to a new gasification event. Thus the effect of He, Ar and N₂ on C-CO₂ gasification rates would be expected to be the inverse of that for C-O₂ gasification rates. Such was not found to be the case experimentally.

To be able to eliminate completely the microscopic heat transfer argument, one should not only consider the over-all gasification reactions but also the first step in both the C-O₂ and C-CO₂ reactions, that is the oxygen transfer step. Indeed, Long and Sykes suggest that the major reason the C-O₂ reaction is much more rapid than the C-CO₂ reaction is because of differences in the oxygen transfer step[12]. They say that since dissociative oxygen chemisorption is exothermic (this is the oxygen transfer step in the C-O₂ reaction), each oxygen atom so adsorbed must possess at first an exceptionally high vibrational energy. After a small number of oscillations and collisions with gas phase molecules, this energy will have been distributed such that the oxygen atom attains the same energy as the mean energy of the solid. However, before the excess energy is dissipated, Long and Sykes suggest that it might be used to overcome the large activation energy required to disrupt the carbon lattice (gasification). For the C-CO₂ reaction the oxygen transfer step is reported by Ergun to be 23 kcal/mole endothermic[13]. Hence, again the microscopic heat transfer argument

cannot explain the similar effects of He, Ar and N₂ on the C-O₂ and C-CO₂ reactions.

Hudgins and Silveston[1] raise another possible explanation for the diluent gas effect, as an extension of Forestier's explanation[14]. They suppose that there is physical adsorption of diluent at an activated complex which loosens the bonds with the solids, permitting more rapid desorption than in the absence of the diluent. Put another way, the interaction of the diluent with the activated complex modifies the potential energy vs distance from the surface path for desorption (gasification in our case) in such a way that the activation energy for desorption is reduced. Hudgins and Silveston[1] rule out this explanation for the diluent effect in the oxidation of SO₂ to SO₃ over V₂O₅. Based on dispersion and repulsion interaction terms, it is estimated that the interaction energies with the activated complex would increase as one goes from He to Ar to Xe[15]. Further, the interaction energy with N₂ should be greater than that of Ar because of quadrupole interaction due to the quadrupole moment on N₂. If greater interaction means a greater weakening of the bonds between the activated complex and the solid, the predicted gasification rates would be in the order Xe > N₂ > Ar > He. Therefore, it seems that this explanation cannot be ruled out in our case, but the explanation lacks firm theoretical justification at this time.

At least one additional, seemingly possible, justification for the diluent effect is proposed by us. It is based on two well-known experimental facts. First, nascent or highly reactive carbon sites are produced continually during carbon gasification. Examples of this phenomenon reported in this laboratory include: (i) an enhanced rate of the C-CO₂ reaction in the presence of desorption of oxygen complex producing CO, where the complex was formed at a lower temperature from O₂[16], (ii) greatly enhanced formation of stable oxygen complex from O₂ while gasification in O₂ occurs as contrasted to where negligible gasification is occurring[17] and (iii) enhanced dissociative chemisorption of chlorine on carbon in the presence of a desorbing oxygen complex compared to chemisorption on a clean carbon surface[18]. Second, is the observation originally by the Mrozowski school[19] that positive holes are formed in carbon by electrons jumping from the π band to the σ state, forming a spin pair at the edge of the crystallite. Or put another way, sp^3 - s^2p^2 rehybridization is expected to occur at some carbon atoms located at crystallite edges[20]. Indeed Coulson concludes that such rehybridization is energetically favored[20]. The net effect is to convert a carbon atom having an unpaired electron on it to one with no unpaired electrons. It is suggested that the nascent sites produced by gasification are those with unpaired electrons on them (sp^3 sites) and at some rate these sites rehybridize to s^2p^2 sites, which are less reactive towards

O₂ and CO₂. Possibly the rate of rehybridization is affected (slowed) by interaction with diluent gases, the greater the interaction the slower the rehybridization rate. If this were the case, rehybridization would be slowest in Xe and most rapid in He. On average, the fewer the nascent carbon sites which have undergone rehybridization before a collision with O₂ or CO₂, the greater should be the collision efficiency for the oxygen transfer step and, hence, subsequent gasification. Thus the gasification rates in the presence of a diluent should be: Xe > N₂ > Ar > He. This is found experimentally for both the C-O₂ and C-CO₂ reactions.

In conclusion, the authors are convinced that there is a diluent gas effect on carbon gasification. An understanding of this effect awaits further theoretical treatment.

Acknowledgements—This study was supported jointly by the U.S. Atomic Energy Commission on Contract No. AT(30-1)-1710 and Aircro Speer Carbon and Graphite.

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