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THE MECHANISM OF CATALYTIC GASIFICATION OF COAL CHAR

By: B. J. Wood, K. M. Sancier,
D. R. Sheridan, B. L. Chan, and H. Wise

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Prepared for:

U. S. DEPARTMENT OF ENERGY
Morgantown Energy Technology Center
P. O. Box 880
Morgantown, West Virginia 26505

Attention: Mr. G. R. Friggens, Project Manager
Mr. John Cunningham, Contracting Officer

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Approved:

D. L. Hildenbrand

D. L. Hildenbrand, Director
Materials Research Laboratory

APPROVED E OR
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333 Ravenswood Ave. • Menlo Park, CA 94025
(415) 859-6200 • TWX: 910-373-2046 • Telex: 334 486

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I INTRODUCTION

Coal gasification is a process of considerable current interest and importance as a source of gaseous fuels and chemical feedstocks. The rates of the gasification reactions are significantly increased by the addition to the coal of certain inorganic salts. Such an enhancement in rate permits gasifier operation at lower temperatures, thus lowering costs and improving the quality of the product gas. To provide a rational basis for the development and improvement of this process, it is necessary to understand the mechanism of action of the catalysts. Consequently, the objective of our study is to determine the mechanisms involved in the catalytic gasification reactions of coal char and to identify the specific reaction steps and the parameters that control the catalytic process.

II EXPERIMENTAL PROGRAM AND RESULTS

Experimental studies in our laboratory, in addition to work reported by others, point clearly to a reaction between the catalyst and carbon as an initial and essential step in the gasification of coal char. This reaction occurs at a solid-solid or solid-liquid boundary, at elevated temperatures, even in the absence of the gaseous feedstocks employed for gasification. However, there is some evidence that this interaction is promoted by the presence of H_2O in an adsorbed state or as a hydrate. The exposure of this catalyst-char mix to a steady stream of steam or carbon dioxide results in a rapid evolution of gaseous products that continues until the carbon is completely gasified. The specific gasification rate increases as carbon is consumed due to the increase in the catalyst/carbon mole ratio.* However, the initial mole ratio K/C is well below unity (typically <0.05) hence the effectiveness of the inorganic material as a gasification catalyst must be maintained by continuous regeneration of its active state.

The mode of action of the catalyst can be viewed in two ways. In one view, the catalyst participates in a reduction/oxidation cycle. The initial reaction between the carbon and the catalyst reduces the KOH to potassium accompanied by the formation of CO and H_2. Subsequently, the potassium is oxidized by the gaseous reactant (H_2O or CO_2), producing further gaseous products (CO and H_2) and regenerating the initial state of the catalyst.

In an alternative view, the catalyst initially forms an alkali metal addition compound with the carbon network of the char. The carbon-carbon bonds are altered by the formation of the metal-carbon linkage, possibly

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*In the case of coal char, some of the catalyst combines chemically with indigenous mineral constituents--a reaction that mitigates the effectiveness of the catalyst.

by electron transfer from the alkali metal atom to the carbon structure. As a result, the carbon structure is more readily attacked by the gaseous reactant (CO or H_2O) to produce the products of gasification.

Before further discussion of these alternative mechanistic pathways, we will examine the experimental evidence.

A. Chemical Kinetic Measurements

Gasification measurements reported earlier[1] demonstrated that K_2CO_3 and KOH are equally effective as catalysts for the steam and CO_2 gasification of both Illinois No. 6 coal char and a pure channel black carbon, Spheron-6. To investigate the possible role of anionic oxygen in the action of the catalyst, we performed experiments with an oxygen-free potassium salt, KBr, impregnated or admixed with the char or carbon. We chose this particular salt because it exists in an anhydrous form under ambient conditions. In addition, one investigator has reported[2] that alkali metal halides impregnated in bituminous coal significantly enhance its rate of steam gasification.

We used the temperature-programmed-desorption/reaction technique (TPD/TPR) to evaluate the reactivity of the halide with Illinois No. 6 coal char and with Spheron-6. The samples were wet-impregnated with KBr to a 10 wt% K level. The apparatus, technique and procedure for these experiments are described in preceding quarterly reports.[1]

When the samples are heated in an inert gas stream at a temperature rise rate of 0.5 $K \cdot s^{-1}$, no gaseous products are observed up to 1200 K. The introduction of 3 vol% steam into the gas stream results in the appearance of CO, CO_2 and H_2 (Figure 1), but at considerably higher temperatures (~1100 K) than those required to produce comparable product emissions with K_2CO_3 or KOH-impregnated carbons (~900 K). The kinetic data obtained in these experiments are summarized in Table 1.

The carbonate and the hydroxide of potassium are highly effective catalysts for char gasification by CO_2. Both CO_2 and H_2O are oxidizing gases. It is of interest whether the rate of reaction of carbon with a reducing gas could be enhanced by these inorganic salts. We performed a TPR experiment in which K_2CO_3-impregnated char was heated in a stream of pure hydrogen. As shown in Figure 2, the rate of production of CH_4 is very low and the presence of the K_2CO_3 causes only a small rate enhancement. No products other than CH_4 were observed in these experiments.

B. Thermodynamic Measurements

Our measurement of the gasification kinetics of KBr-impregnated char is being supplemented with an examination of the vapor species in equilibrium with the char under gasification conditions. For this investigation, we use high-temperature Knudsen cell mass spectrometry, described in detail in previous reports.[1,3]

1. Pure Potassium Bromide

For the current series of experiments, the system was calibrated with a 100 mg sample of pure KBr in the Knudsen cell. The measurement of KBr^+ ion intensity above this pure solid, as a function of cell temperature in the range 730-863 K, provided an absolute pressure reference scale for the quadrupole mass spectrometer. The observed ion intensity, I^+, is related to the pressure, P, of the gaseous species by the following equation:

$$P = \frac{k\, I^+ T}{\sigma} \qquad (1)$$

where T is the absolute temperature and σ is the relative ionization cross-section. The results of vaporization measurements on the KBr sample are plotted in Figure 3.

The enthalpy of vaporization, ΔH_T, evaluated from these data is 193.3 $kJ \cdot mol^{-1}$. This value is in agreement with the accepted value[4] of $\Delta H_T = 204.6\ kJ \cdot mol^{-1}$. Also, the observed abundance of the dimer species, K_2Br_2, relative to that of the monomer KBr, corresponded to the accepted value. These observations verify that the partial pressures of species emanating from the Knudsen cell are truly representative of their equilibrium values within the cell (that is, in contact with the solid phase).

The mass spectrometer pressure calibration with KBr was extended to other species by

(1) maintaining identical constant instrument settings for all runs.

(2) using an ionizing energy at a fixed level relative to each species' ionization potential.

In accordance with the convention adopted in previous experiments, we measured each ion signal using an ionizing energy of 3.5 eV above its ionization potential. The use of such a modest ionizing energy greatly minimizes the contributions of fragment ions to the mass spectra.

2. Carbon Plus Potassium Bromide

A 130 mg sample of a mineral-free carbon, Spheron-6 channel black, containing 4 wt% K as KBr was loaded into a graphite Knudsen effusion cell. This sample had been prepared by impregnation with aqueous KBr and subsequently pretreated by heating overnight in vacuo at 580 K. Upon further warming of the sample in the Knudsen cell, we observed HBr evolution at 650 K. No other potassium-containing species were discerned. The HBr was accompanied by CO and CO_2 and by a weak evolution of H_2O. As in the case of other carbon and char samples,[1,3] these H_2O, CO, and CO_2 peaks apparently originated from strongly-bound absorption states in the Spheron-6. The evolution of HBr, however, was indicative of a hydrolysis reaction occurring between H_2O and KBr. At constant temperature HBr evolution decreased with time, although the KBr^+ signal was stable.

We measured the temperature dependence of the KBr^+ signal in the range 721-842 K. The results of these measurements are shown in Figure 3. The observed pressures of KBr above the KBr-impregnated Spheron-6 sample agree closely with those over pure KBr. This behavior indicates that there is no interaction between KBr and Spheron-6 in the temperature range investigated.

To further investigate the appreant hydrolysis reaction between KBr and H_2O in the presence of carbon, we performed a second experiment. A fresh sample of Spheron-6 was dried by heating in a stream of inert gas (Ar) overnight at 1073 K. The Spheron-6 was cooled to room temperature in the inert atmosphere. Subsequently, a portion of this carbon was quickly weighed, ground briefly in a mortar with an appropriate mass of KBr to prepare a 4 wt% K sample and promptly loaded into the Knudsen cell. Upon heating in vacuo, CO, CO_2 and H_2O evolution commenced at about 400 K, but as the temperature was further raised, the partial pressures of these gases remained significantly lower than those observed in the previous experiment. Also, HBr evolution was less than 10% of the previously observed levels. Values of KBr pressure above this sample, shown in Figure 3, are in close agreement with those observed above for KBr. As in the experiment with the solution-impregnated carbon, KBr and K_2Br_2 were the only potassium-containing species detected in the vapor above the sample.

3. Effect of Added CO_2 and H_2O

A 130 mg sample of predried Spheron-6 ground together with 4 wt% K as KBr was loaded in a graphite Knudsen cell with a graphite gas inlet tube.[3] This sample was not pretreated by overnight heating at 580 K in vacuo. Instead, it was heated at a relatively rapid rate to reach 800 K in about 7.2 Ks. During this heating period maxima in the evolution rate of CO_2 and H_2O were observed at $T \approx 470$ K and $T \approx 540$ K, respectively. No HBr^+ signal was detectable at any observed temperature, although a weak H_2O^+ signal was present even at 780 K. The level of KBr^+ signal at this temperature was approximately a factor of three lower than that observed in the preceding experiments. Such a depression in the KBr^+ level may be due to kinetic limitations associated with the relatively rapid rate of heating the sample.

When steam was added through the gas inlet system to raise the total H_2O pressure within the cell to 10^{-3} Pa, an immediate 15% decrease in the KBr signal occurred. No other potassium-containing species were detectable.

During sustained and constant flow of H_2O (g) through the cell for 1800 s, the KBr^+ signal level dropped by 50%. Spot measurements at several temperatures for various durations of flow indicated that the KBr pressure contained to decrease during exposure to steam (Table 2). To better illustrate the effect of steam we evaluated the ratio $P_{KBr\ observed}/P_{KBr\ equilib}$. The value of this ratio decreases monotonically with an increasing duration of steam exposure, but begins to recover when the steam supply is interrupted (Table 2).

At T = 945 K in the presence of steam a K^+ peak appeared in the mass spectrum and began to grow steadily. Discontinuance of the steam supply caused this peak to decrease. The behavior of this gaseous species at 985 K is shown in Figure 4. The addition of steam to the cell also resulted in the appearance of CO and CO_2 .

C. Free Radicals in Reacting Carbon

As a probe of the reactive solid phase in char gasification, we have made extensive use of electron spin reasonance spectroscopy (ESR) to measure the concentration and chemical environment of free radicals under gasification conditions. The apparatus and experimental techniques used for these in situ measurements are described in detail in preceding reports.[1,3]

We have extended our earlier work to investigate

(1) possible interactions between the free radicals of carbon and a series of potassium salts that might have different catalytic gasification activities, and CaO, which is a relatively poor catalyst.

(2) the effect of CO_2 gasification on the free radicals in carbon-salt mixtures.

The potassium halide salts (KF, KCl, KBr, and KI) and K_2CO_3 were chosen to investigate the effect of various anions on the catalytically important K^+ ion. We selected these salts because KF has been reported[5] to be considerably more active than KCl for the CO_2 gasification of graphite. Calcium oxide is of interest because it is a relatively poor gasification catalyst[6] and therefore can be used as an inert diluent or support to examine the ESR behavior of carbon. Also, CaO is one of the few substances of catalytic interest whose metal ion does not have a nuclear magnetic moment. Consequently, the ESR spectra would be free of line broadening effects attributable to electron-nuclear hyperfine interaction between the Ca^{++} and unpaired electrons associated with carbon.

In the current experiments, the reactor tube was loaded with 50 mg of a mechanically ground mixture containing 3 wt% carbon (Spheron-6) in a given salt. The purpose of using a dilute mixture of carbon in a salt is to minimize the microwave skin effect due to intergranular electrical conductivity among carbon particles which causes unsymmetrical ESR lines. For these dilute samples, we always observed symmetrical lines. Preliminary to ESR measurements the sample was heated to about 500 K in flowing He to desorb O_2. Subsequently, ESR measurements were made at various temperatures in the range 290 - 950 K after allowing time (~600 s) at each point for thermal equilibrium to be established. A switching valve permitted the gas composition passing over the sample to be instantly shifted between He and one of several mixtures of He and CO_2 (4.1, 7.9, and 15.8 vol% CO_2, respectively).

In previous reports, only relative free radical concentrations were given. Now, however, we have quantified our ESR results by using a first moment analysis of the first derivative ESR curve to evaluate free radical concentrations. For this analysis, a computer was used to digitize the real-time data and later to perform the first moment computation. A sample of 0.1% pitch in KCl (Varian) served as a calibration standard. The results were normalized for temperature (according to a Curie law) and for cavity sensitivity, which depended strongly on sample temperature. Indeed, when the temperature was raised from 300 to 940 K, cavity sensitivity dropped to 11%. Relative cavity sensitivity was obtained from the peak-to-peak height, I_p, of the resonance due to the pitch sample located in the reference section of the microwave cavity.

1. Thermal Effects

In flowing He the effects of increasing sample temperature on the ESR line width and the free radical concentration are shown in Figures 5 and 6. Measurements of line width were made while increasing the temperature (Figure 5a) and also at 290 K after cooling from each progressively higher temperature (Figure 5b). The results show that the line width increased with increasing temperature above 600 K and was greater at a given elevated temperature than when cooled to 290 K. The broadening effect for various carbon-salt mixtures at a given temperature increased in the following order: $CaO < KF < K_2CO_3 < KI \approx KCl \approx KBr$.

The effect of temperature on the free radical concentration is shown in Figure 6a and for the sample cooled to 290 K from a given temperature in Figure 6b. The results indicate that the free radical concentration increased with increasing temperature above $\sim$ 700 K and was greater at a given elevated temperature than when the sample was cooled to 290 K. The free radical concentrations for various carbon-salt mixtures at a given temperature exhibited about the same order observed for the line width.

The values of the line width and free radical concentrations are not strictly equilibrium values, because at given elevated temperatures (e.g., $T > 800$ K) both of these parameters slowly increased with time. Evidently, these increases result from chemical reactions that occur at high temperatures, possibly polymerization of carbon or pyrolysis. For reference purposes we determined that in the absence of carbon, free radicals were not produced thermally in the salts K_2CO_3 or KBr.

2. Effects of CO_2

To evaluate the effects of CO_2 gasification conditions on the ESR spectrum of carbon-K_2CO_3 mixture, the flowing gas was switched back and forth between He and one of the three mixtures of He containing CO_2 in separate experiments at two temperatures, 800 and 850 K. The data points obtained (Figures 7 and 8) are numbered to indicate the measurement sequence, with the odd numbered points representing pure He. The results indicate that the ESR free radical line was narrowed when CO_2 was present and broadened when He alone was flowing (Figure 7). Also, at both temperatures the line width measured in He was increased by prior exposure of the sample to CO_2. However, the free radical concentration gradually decreased during the higher temperature experiment (See Figure 8). This decrease may be due to chemical changes in the solid such as loss of carbon or polymerization of free radicals.

A similar set of experiments was performed with samples of carbon in KBr and in CaO at 780 K. No changes in either line widths or free radical concentrations could be detected when the flowing gas was switched between He and 15.8% CO_2 in He.

We wish to emphasize at this point the importance of making in situ ESR measurements in char studies, because the character of the free radicals differs greatly between reacting conditions and after the sample is cooled. Also, it is imperative to correct the free radical concentrations for changes in the ESR cavity sensitivity with temperature (due to variation of electrical conductivity of the samples).

D. Electrical Conductivity Measurements

To gain a better understanding of the interaction between alkali metal catalysts and the carbon network encountered in coal char, we carried out a series of electrical conductivity measurements. For this purpose samples of a devolatized Illinois #6 coal char with and without K_2CO_3 catalyst were pressed into pellets and clamped between two electrodes made from high temperature graphite rods (grade ATJ, Union Carbide Corporation). Direct current conductivity measurements[7] in a He atmosphere were carried out after it had been established that the contact between electrodes and sample was ohmic (i.e., little contact resistance). The general behavior of the samples examined is shown qualitatively in Figure 9. In the absence of K_2CO_3 the coal char sample exhibits a small decrease in conductivity with rising temperature (Curve B, Figure 9). However, the catalyst-impregnated sample exhibits quite different behavior. The conductivity increased with rising temperature and a marked change in the slope of the curve (A in Figure 9) occurred near 500 K. Of special interest is the lack of reversibility of the conductivity with temperature. A lowering of the sample temperature yields curve A' (Figure 9) indicating only a small change in the high conductivity attained. In this high-conductivity regime, the addition of 4 vol% CO_2 to the He atmosphere caused a measurable reduction (~10%) in the electrical conductivity. Nearly identical curves were obtained with K_2CO_3-impregnated carbon black (Spheron-6) samples.

III DISCUSSION

A. The Catalyst-Carbon Interaction

There is some evidence that H_2O serves as a catalyst activator by converting the various potassium salts to KOH. The liberation of CO_2 at about 420 K in TPD experiments with K_2CO_3-impregnated samples,[8] appears to be a consequence of hydrolysis of the carbonate. The source of H_2O for this reaction in these experiments must reside within the solid sample as water of hydration in the salt or as adsorbed water in the char. We reach this conclusion because the amount of CO_2 liberated at this temperature is greatly diminished for samples which have been dried by heating for long periods at 385 K prior to the TPD experiment.

A similar liberation of CO_2 was observed in the Knudsen cell mass spectrometry experiment[3] with K_2CO_3-impregnated char. Observations with this technique demonstrate also the hydrolysis of KBr in KBr-impregnated carbon samples by the appearance of HBr at $T > 650$ K. Most likely water originates from the adsorbed state on the solid carbon, because KBr does not form a hydrate. The affinity of activated carbon for H_2O was vividly demonstrated by the appearance of HBr over a mixture of devolatized carbon and anhydrous KBr that had been exposed to the ambient atmosphere for only a few minutes prior to evacuation in the Knudsen cell apparatus.

The particular efficacy of KOH as a catalyst may reside in part in the low melting point of this compound relative to the carbonate and the halides ($MP_{KX} - MP_{KOH} > 300$ K). Microscopic observations in our laboratory[9] and reports from other investigators[10,11] have indicated that extensive and intimate contact between the char and the catalyst is an essential prerequisite to high activity. Liquefaction of the catalyst at a low temperature provides a means for rapid spreading of the catalyst over the surface of the solid carbon.

The experimental evidence suggests that both the potassium halides and the carbonate are readily hydrolyzed at or below gasification temperatures. Yet the carbonate exhibits substantially greater catalytic activity for gasification than do the halides. The reason for this disparity likely lies in the high volatility of the halide salts relative to KOH. Gaseous KBr was the major species in equilibrium with KBr-carbon mixtures at temperatures several hundred degrees below the region where gasification rates become measurable. Although hydrolysis of KBr is observed at low temperatures, the rate of vaporization of the halide may be more rapid than hydrolysis under our experimental conditions, thus depleting the concentration of the potassium salt in the solid phase and mitigating the potential for activation of the carbon.

Both kinetic (TPD) and thermodynamic (Knudsen cell mass spectrometry) measurements give substantial evidence for a solid-state chemical interaction between KOH and carbon. The gasification rates, as reflected by the TPD spectra, are essentially identical for 10% K impregnated in Illinois No. 6 coal char whether in the form of K_2CO_3 or KOH. In both cases CO_2, CO, and H_2 appear as products in the temperature range 900-100 K. In the Knudsen cell experiments[2] K(g), CO_2, and CO were the detected vapor species [H_2 (AMU=2) was outside the observed mass range]. The equilibrium partial pressure of K(g) over the catalyst-impregnated char was greater than that observed over pure K_2CO_3 yet less than that predicted from the published equilibrium data[4] for the reduction of potassium carbonate by carbon:

$$K_2CO_3(s) + C(s) = 2K(g) + CO_2(g) + CO(g).$$

The potassium-containing solid phase in the Knudsen cell exhibits a unique value of thermodynamic activity for potassium (at a given temperature), possibly indicative of a new chemical compound formed by the interaction between potassium and carbon. The nature of this compound, possibly a reaction intermediate, is of considerable importance in understanding the mechanism of the gasification reactions.

B. The Reaction Intermediate

Addition of steam or CO_2 to a Knudsen cell that contained K_2CO_3-impregnated char substantially reduced the equilibrium partial pressure of K(g). Interruption of the gaseous reactant stream after a prolonged period of flow[3] resulted in only partial recovery of the initial partial pressure of K(g). The reversible portion of the potassium vapor suppression by steam or CO_2 likely is due to homogeneous chemical reaction between the K(g) and the added gas. The subsequent, slow, nearly irreversible supporesion must be attributed to permanent changes in the solid phase in the cell. Gasification, of course, depletes the mass of the carbon phase and, with time, leads to a condition where the original solid catalyst phase can reappear. In such a situation, the K(g) pressure would be substantially reduced, as indicated by the dissociation pressure of the pure salt. Also, in the case of mineral-containing chars, potassium can be converted to nonvolatile silicates or alumino silicates. In any event, the potassium must be intimately associated with the carbon solid phase. This notion is reinforced by the observation of broad ESR free radical lines in the K_2CO_3-impregnated carbon samples. The cause of line broadening may be hyperfine splitting due to interaction of an unpaired electron associated with the carbon with the nuclear magnetic moment of the potassium -- a process that requires close proximity of the electron and the potassium atom. Within this constraint, two distinct models for a reactive intermediate species may be postulated: A redox cycle model and a potassium addition compound model.

1. Redox Cycle Model

If the mechanism of gasification involves simple oxidation-reduction cycling of the catalyst with the solid char performing as the reducing agent and the gaseous reactant (CO_2 or H_2O) as the oxidant, the reduced state of the catalyst might consist of a separate phase in contact with the carbon. Such a phase would likely be a liquid distributed extensively over the carbon surface (perhaps only a few atomic layers thick) and have the composition of a nonstoichiometric potassium oxide, KO_x. Free energies of formation have been measured[12] for liquid melts in the potassium-oxygen system in the composition range O/K = 0.5 to 1.75 and in the temperature range 773 to 923 K. The O/K ratio in the liquid phase diminishes monotonically as the oxygen partial pressure is reduced. This type of behavior suggests that, under strongly reducing conditions, such as in contact with elemental carbon, oxygen ion vacancies may be created in the liquid phase. The equilibrium vapor pressure of potassium over a particular oxygen-deficient oxide phase would be altered, and would exhibit variation with temperature different from that of stoichiometric potassium oxide, as observed in our Knudsen cell mass spectrometric measurements.

Reduction of an oxide to a nonstoichiometric composition (i.e., removal of $O^=$ ions from the lattice) will provide free electrons as electrical charge carriers. Consequently, the electrical conductivity of the oxide is enhanced in proportion to the concentration of electrons and their mobility in the lattice.[13] Reaction with an oxidizing gas such as CO_2 or steam would tend to fill the $O^=$ vacancies and reduce the electrical conductivity of the phase. Such behavior is consistent with our observations of electrical conductivity changes in K_2CO_3-impregnated char.

The formation of such a phase is generally consistent, also, with the loss in surface area that occurs when the impregnated char is heated.[9] Because reaction with the gaseous oxidant (H_2O or CO_2) could occur at the surface of the liquid melt and not necessarily at the carbon-liquid interface, the reaction rate would be insensitive to char surface area, as observed in our experimental measurements.[9] Finally, the fact that the hydrogasification rate is not enhanced significantly by the addition of catalyst to the char strongly supports the mechanism in which a redox cycle is the specific reaction pathway.

In principle, we can estimate the composition of a nonstoichiometric liquid oxide phase in contact with the char from the equilibrium partial pressures of K(g), CO, and CO_2 observed in our Knudsen cell experiments and the reported[12] free energies of formation of liquid melts with various oxygen/potassium ratios.

At equilibrium, the potassium/oxygen compound on the char is in contact with the gaseous components in accordance with the following equation:

$$K_{(1+x)}(\ell) + C(s) = K(g) + xCO_2 + (1 - x)CO \tag{1}$$

The free energy change ΔG of this reaction is the difference between the standard free energies of formation, ΔG_f^o (i) of the products and reactants, i :

$$\Delta G = x\Delta G_f^o\ (CO_2) + (1 - x)\Delta G_f^o\ (CO) - \Delta G_f^o\ (KO_{(1+x)}) \tag{2}$$

Also, since the liquid phase will exhibit unit thermodynamic activity at a temperature, T :

$$-\Delta G = RT\ \ln(P_{CO}^{(1-x)} \cdot P_{CO_2}^{x} \cdot P_K) \tag{3}$$

where P_i is the partial pressure of gaseous species i and R is the gas constant. Combining equations (2) and (3), we obtain

$$\Delta G_f^o(KO_{(1+x)}) - x\Delta G_f^o(CO_2) - (1-x)\Delta G_f^o(CO) = RT\ \ln(P_{CO}^{(1-x)} \cdot P_{CO_2}^{x} \cdot P_K) \tag{4}$$

Using our experimental values of P_i (Ref. 1, Table 4), standard free energies of formation for CO and CO_2 from Reference 4, and values of ΔG_f^o $(KO_{(1+x)})$ from Reference 12, we solved equation (4) numerically for x. A real root solution could not be obtained, which suggested that the liquid phase might possess an O/K ratio lower than 0.5 for which free energy values are not available. However, the existence and thermodynamic properties of suboxides of rubidium and cesium under reduced oxygen pressure have been reported[14]. By analogy to these alkali metals, it is not unreasonable to expect that the potassium-oxygen system can exhibit similar states.

X-ray photoelectron spectra (XPS) of K_2CO_3-impregnated carbon[15] exhibit a downscale energy shift of about 1 eV in the 2p lines of potassium when the sample, heated to 923 K in vacuo, is exposed to O_2 or CO_2 at a pressure of 53 Pa. Such line shifts, indicative of changes in the binding energy of the 2p electrons, are sensitive indicators of the chemical environment and state of the element.[16] To our knowledge, no XPS data have been reported for the potassium-oxygen system.[17] However, oxides of another alkali metal, cesium, have been subjected to XPS examination.[14] The binding energy of the 3d electrons in cesium metal is about 1 eV greater than that in Cs_2O. Thus, the alkali metal core electrons are more strongly bound in the metal than in the oxide. If, by analogy, we extend this characteristic to potassium, the XPS data suggest that the potassium in the char is converted to a reduced state by reaction with the carbon and conversely it becomes associated with an oxide upon exposure to an oxidizing gas.

Also, ultraviolet photoelectron spectra (UPS) of Cs and Rb suboxides exhibit partly occupied conduction bands indicative of a metallic character of the solid.[14] These substances are further characterized by very narrow oxygen 2p bands. Such narrow bands may be associated with weak binding and high mobility of the $O^{=}$ ions in the suboxide lattice. Very narrow O 2p bands have been reported[18] for potassium during early stages of oxidation, even though bulk suboxides of this element are not yet known.

All of this information lends support to the existence of an oxygen-deficient potassium oxide phase that mediates a redox cycle involving the solid carbon and the oxidizing gas in the catalytic gasification of coal char.

2. Potassium Addition Compound Model

On the basis of the available experimental evidence, we cannot dismiss an alternative reaction model in which the potassium salt initially decomposes by reaction with the carbon structure to form a potassium-addition compound. The addition compound represents the active intermediate that is directly attacked by the gaseous oxidant to form the reaction products. The addition compound may be characterized by the formation of a covalent bond between the carbon and potassium, or by electron transfer to the carbon structure from the potassium, which then assumes the role of a counter ion. The high reactivity of such a carbon structure toward CO_2 and H_2O may not be exhibited with H_2, because there is no surface on which dissociation of the H_2 molecule can occur. However, such an addition compound could be a free radical that would exhibit an ESR free electron resonance line and an enhanced electrical conductivity. In addition, such a compound might possess a unique potassium dissociation pressure in the gasification temperature regime.

We will discuss the possible nature of the addition between K and the carbon structure, with particular reference to the observed ESR behavior of catalyzed carbon. It is likely that K is bonded to the carbon structure either directly to a carbon-atom (----C-K), or through an oxygen atom (---C-O-K).[19] The nature of the bond may be mainly ionic or partially covalent. Magnetic resonance experiments[20] show that the atomic character of potassium in aromatic radical anions is less than 3.0%, (i.e., the bond is mostly ionic), in contrast to an atomic character as high as 46% for the case of potassium in isopropylamine. These two cases correspond to electron-nuclear hyperfine coupling constants of 0.2 and 3.5 mT (2 and 35 Gauss), respectively. Potassium-coal adducts have been reported[21] to exhibit ESR line widths of 0.44 to 0.66 mT. In our measurements, ESR line widths between 0.4 and 5.0 mT were observed for admixtures of carbon and various potassium salts at 950 K (Figure 5). We postulate that the mechanism of ESR line broadening that we observe is due to an unresolved hyperfine interaction between the unpaired electron of the free radical and the nuclear magnetic moment of the metal atom. An alternate line broadening mechanism is a magnetic dipolar interaction among unpaired electrons at high concentration. However, this mechanism offers a rather unsatisfactory explanation for our results, particularly those where very broad lines are associated with relatively small free radical concentrations. For example, an observed line width of 5.0 mT at a free radical concentration of 1.5×10^{21} radicals/g carbon cannot be reconciled with a line width of 0.44 mT reported[21] for potassium-coal adducts with radical concentrations of 3×10^{21} per g carbon, on the basis of a magnetic dipole interaction broadening mechanism. To produce strong hyperfine interactions, i.e., broad ESR lines, the distance of separation between the metal atom and the carbon structure containing the radical electron must be very small. Theoretical calculations have been made of the electrostatic attraction between radical anions and sodium cations. These results indicate that the sodium ion may be positioned about 3 Å above the nuclear plane of the radical anion (naphthalenide or anthracenide).[22] A map of the unpaired electron density has been made from ESR measurements and higher densities are calculated to exist about certain carbon-carbon bonds in Na-aromatic anion radicals. The extent of localization of electron density, as well as the atom character of metal atoms, will depend on several factors including: the nature of the carbon structure, the electron affinity of its anion radical, the type of metal atom, solvent effects (nearest neighbor effects in solids), and temperature.

In a discussion of catalytic gasification of coal, Wen[23] proposes that the C-K bond polarizes the electron density in the aromatic carbon structure so that the C-C bond adjacent to the C-K group is weakened and made more reactive toward CO_2 or H_2O. We propose that the free radicals we observed by ESR in heated carbon-potassium mixtures are due to carbon structures in which the potassium-carbon bond is more covalent than in the radical anion examples referred to above.[21] The formation of these bonds by effective catalysts, such as K_2CO_3, causes weakening of adjacent C-C bonds in the carbon network. When such C-C bonds in an aromatic ring are ruptured thermally, the aromatic structure is transformed into very reactive aliphatic fragments. These fragments are free radicals which account for the observed increase in the ESR spin density. In an inert atmosphere, these aliphatic fragments can polymerize so that the unpaired electron concentration is rapidly diminished. However, residual aliphatic-type radicals will exhibit small ESR line widths because the associated unpaired electrons cannot interact with potassium as readily as in an aromatic structure. In this way we may account for the observation that the free radical concentration and line width are smaller for a good catalyst such as K_2CO_3 than for a poorer catalyst, such as KBr. An ineffective salt, such as CaO, will not accelerate thermal decomposition of the carbon structure; consequently, the free radical concentration in this case is not increased very much upon heating.

To account for the ESR results observed during gasification (higher free radical concentrations and reduced line widths) we hypothesize that the oxidizing gas reacts with the thermally produced and reactive aliphatic fragments. During gasification, the observed increase in free radical concentration is apparently due to the multiple rupture of carbon-carbon bonds in the aromatic carbon network, with the formation of aliphatic free radical fragments. The decreased ESR line width is a consequence of the formation of these radical species because the possibility for electron-nuclear interaction between unpaired electrons in an aliphatic structure is much less than in an aromatic network.

The observation that the catalytic activity for CO_2 gasification of carbon by potassium salts appears to depend on the anion of the salt may be related to the volatility of the salt or to the presence of water in the salt, as discussed earlier. Among the K salts studied by ESR, only those that form hydrates, viz, $KF \cdot 2H_2O$ and $K_2CO_3 \cdot 2H_2O$, exhibit high activity for gasification.

The present ESR results on CO_2 gasification are qualitatively analogous to those on steam gasification reported earlier for carbon-K_2CO_3.[1,3] Both reactive gases, CO_2 and H_2O, caused the ESR line width of the carbon resonance to decrease, but the effect with H_2O appeared to be more reversible. The qualitative similarities between CO_2 and steam gasification on the ESR spectra of carbon/K_2CO_3 mixtures suggests that the same free radicals are reacting with the CO_2 and H_2O, and that the same mechanism accounts for changes in ESR line width and free radical concentrations.

Our d.c. conductivity measurements lend themselves to a similar interpretation. For the catalyst-containing sample at room temperature, the large difference in conductivity of more than two orders of magnitude between the starting material and the final state indicates a large modification in the solid state properties of the sample. Possibly the observed change results from the formation of electron-transfer bonds between the potassium and the carbon network of the char, analogous to the alkali metal-hydrocarbon complexes observed during the interaction of alkali metals with anthracene[24] and coal.[25] The break in the conductivity curve near 500 K coincides with measurable interaction between the catalyst and the char, as evidenced by the evolution of CO_2 and H_2O. Samples of Spheron-6 containing K_2CO_3 exhibit similar behavior to that observed with coal char. It is of interest that the high conductivity of the coal char (Figure 9, curve A') is greatly diminished by exposing the sample to room air. Undoubtedly the K-carbon polymer complex is affected by either O_2 or water vapor from the atmosphere. However, it can be restored by heating in He (i.e., retracing curve A of Figure 9).

IV FUTURE WORK

During the next quarter, we plan to emphasize the following areas:

(1) Examine the interaction with char of salts containing different cations and anions, with particular attention to the role of adventitious water.

(2) Commence experiments with different chars to determine effects associated with relative volatility, mineral content, etc.

V PERSONNEL

Staff members who have contributed to this project during the reporting period include:

C. M. Ablow
Robert Brittain
Robert Lamoreaux
Steve Leach
Jon McCarty
Kenneth Sancier
David Sheridan
Henry Wise (Project Supervisor)
Bernard Wood (Project Leader)

REFERENCES

1. B. J. Wood, et al., "The Mechanism of Catalytic Gasification of Coal Char," SRI International, DOE Contract No. AC21-80MC14593, Quarterly Technical Progress Report No. 2 (April 15, 1981).

2. W. P. Haynes, S. S. Gasior, and A. J. Forney, pp. 179-202 in Coal Gasification, L. G. Massey, ed., American Chemical Society Advances in Chemistry Series No. 131, Washington, DC (1974).

3. B. J. Wood, et al., "The Mechanism of Catalytic Gasification of Coal Char," SRI International, DOE Contract No. AC21-80M14593, Quarterly Technical Progress Report No. 3 (August 15, 1981).

4. JANAF Termochemical Tables, NSRDS-NBS, 37, 2nd edition, U. S. Government Printing Office, Washington, DC (1971).

5. P. G. Kosky, et al., "Coal Gasification Catalysis Mechanisms," General Electric Corporation Research and Development Center, DOE Contract No. DE-AC21-80MC14591, Quarterly Progress Report No. 4 (June-September, 1981).

6. W. P. Haynes, S. J. Gasior, and A. J. Forney, ACS Reprints of Papers, 165th Meeting, Div. Fuel Chem., 18(2) (April 1973).

7. H. Wise, J. Phys. Chem., 71, 2843 (1967).

8. B. J. Wood, et al., "The Mechanism of Catalytic Gasification of Coal Char," SRI International, DOE Contract No. AC21-80MC14593, Quarterly Technical Progress Report No. 1 (January 19, 1981).

9. B. J. Wood, et al., "The Mechanism of Catalytic Gasification of Coal Char," SRI International, DOE Contract No. AC21-80MC14593, Quarterly Technical Progress Report No. 4 (November 15, 1981).

10. D. W. McKee and D. Chatterji, Carbon 13, 381 (1975); ibid 16, 53 (1978).

11. B. P. Jalan and Y. K. Rao, Carbon 16, 175 (1978).

12. A. J. Leffler and N. W. Wiederhorn, J. Phys. Chem. 68, 2882 (1964).

13. P. Kofstad, Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides, pp. 28ff (New York: Wiley Interscience, 1972).

14. A. Simon, Struct. Bonding (Berlin), 36, 81 (1979).

15. S. Yokoyama, K. Tanaka, I. Toyoshima, K. Miyahara, K. Yoshida and J. Tashiro, Chem. Lett., No. 5, 599 (1980).

16. D. M. Hercules, Anal. Chem., 42, 26A (1970).

17. L. R. Scharpen, private communication.

18. L. G. Peterssen and S. E. Karlsson, Proc. 5th Intl. Conf. Vacuum Ultraviolet Radiation Physics, Vol. II, 253 (1977).

19. C. A. Mims and J. K. Pabst, Am. Chem. Soc. Div. Fuel Chem. Preprints, 25 (3), 258, 263 (1980).

20. N. L. Holz, Chem. Rev. 74 (2) 243 (1974).

21. L. Lazarov and M. Stefanova, Fuel 60, 723 (1981).

22. I. B. Goldberg and J. R. Bolton, J. Phys. Chem. 74, 1965 (1970).

23. W-Y Wen, Catal. Rev. - Sci. Eng. 22, 1 (1980).

24. W. A. Holmes-Walker and A. R. Ubbelohde, J. Chem. Soc. (London), 720 (1954).

25. H. W. Sternberg and C. L. Delle Donne, Fuel, 53, 172 (1974).

Table 1

GASIFICATION RATES OF CHAR AND CARBON AT 1023 K

Solid Reactant	Gaseous Feedstock	Catalyst	Loading wt% K	Initial Specific Carbon Gasification Rate s^{-1}
Illinois No. 6 Coal Char	3 vol% steam	none	0	$<5 \times 10^{-6}$
		K_2CO_3	8	9.0×10^{-4}
			4	2.9×10^{-4}
		KOH	8	9.6×10^{-4}
		KBr	4	1.2×10^{-5}
	3 vol% CO_2	none	0	$<5 \times 10^{-6}$
		K_2CO_3	8	3.0×10^{-4}
Spheron-6 Channel Black	3 vol% steam	none	0	$<5 \times 10^{-6}$
		K_2CO_3	8	6.0×10^{-4}
		KBr	4	1.6×10^{-5}
	3 vol% CO_2	K_2CO_3	8	3.7×10^{-4}

Table 2

EFFECT OF STEAM ON EQUILIBRIA IN THE KBr-CARBON SYSTEM[a]

Temperature (K)	Duration of Exposure to Steam[b] (s)	I_{KBr^+} (mV)	$\frac{P_{KBr}\text{ observed}}{P_{KBr}\text{ equilib.}}$[c] (x 10^2)
779	0	4.60	29
	300	4.00	26
892	1800	114	17
907	2100	60	5.9
945	2400	80	2.8
983	~2400[d]	345	5.0

[a] Mechanical mixture of 4% K as KBr with Spheron-6 channel black.

[b] $P_{H_2O} \approx 10^{-3}$ Pa.

[c] Ref. 4 and Fig. 3.

[d] Steam supply cut off after point at T = 945 K had been recorded.

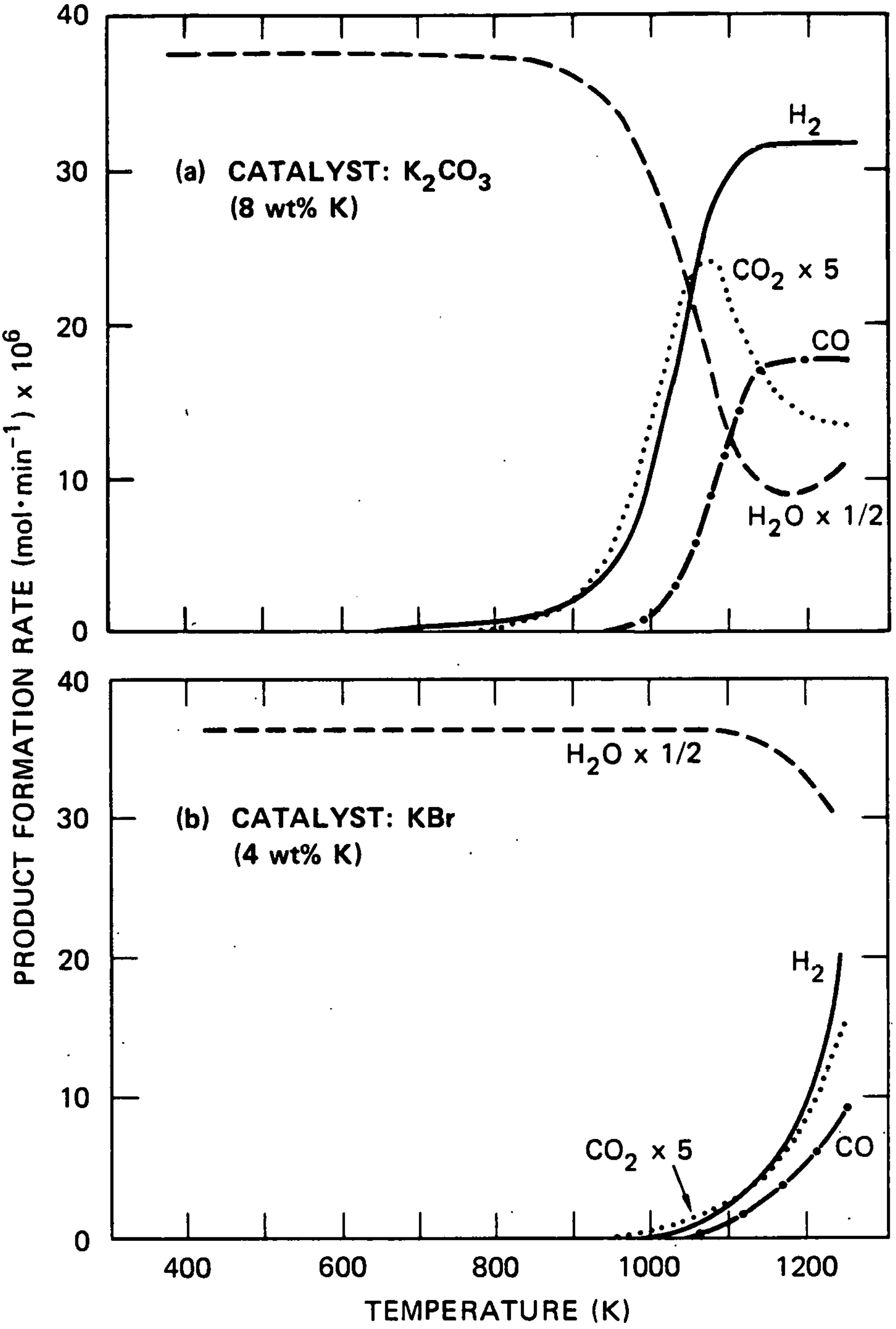

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FIGURE 1 TPR PRODUCT SPECTRA

Illinois No. 6 coal char heated in H_2O/He = 3.1/98 (kPa/kPa); flow rate: 1 cm^3 s^{-1}; temperature ramp: 0.5K s^{-1}.

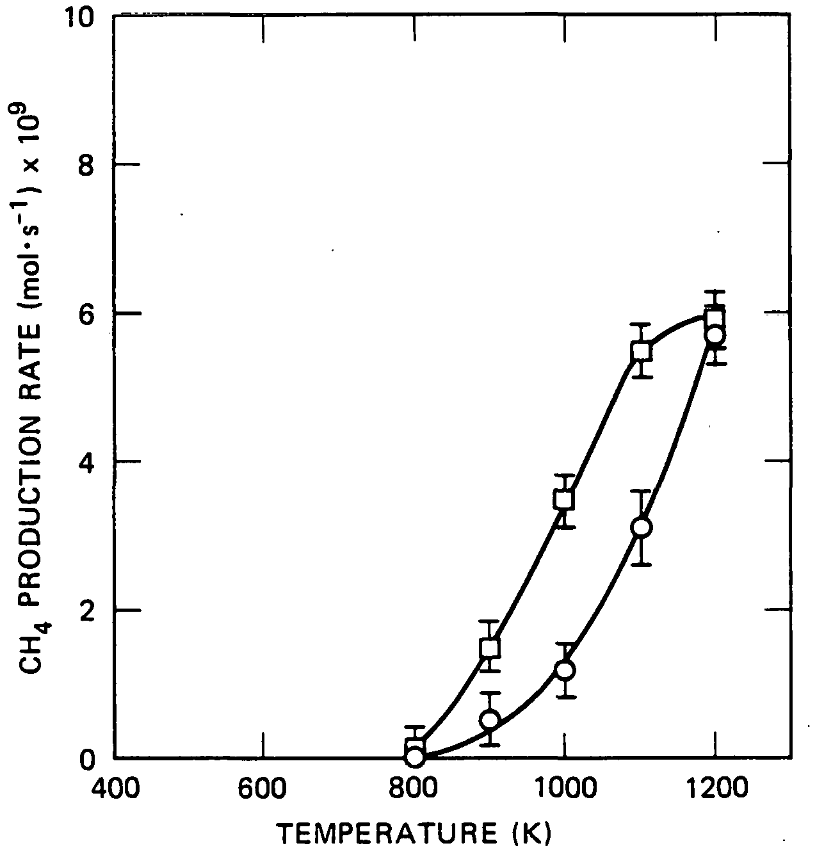

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FIGURE 2 EVOLUTION OF CH_4 DURING TPR IN H_2

Illinois No. 6 coal char; temperature ramp: 0.5 K s^{-1}.
○ No catalyst; □ Catalyst (8 wt % K as K_2CO_3).

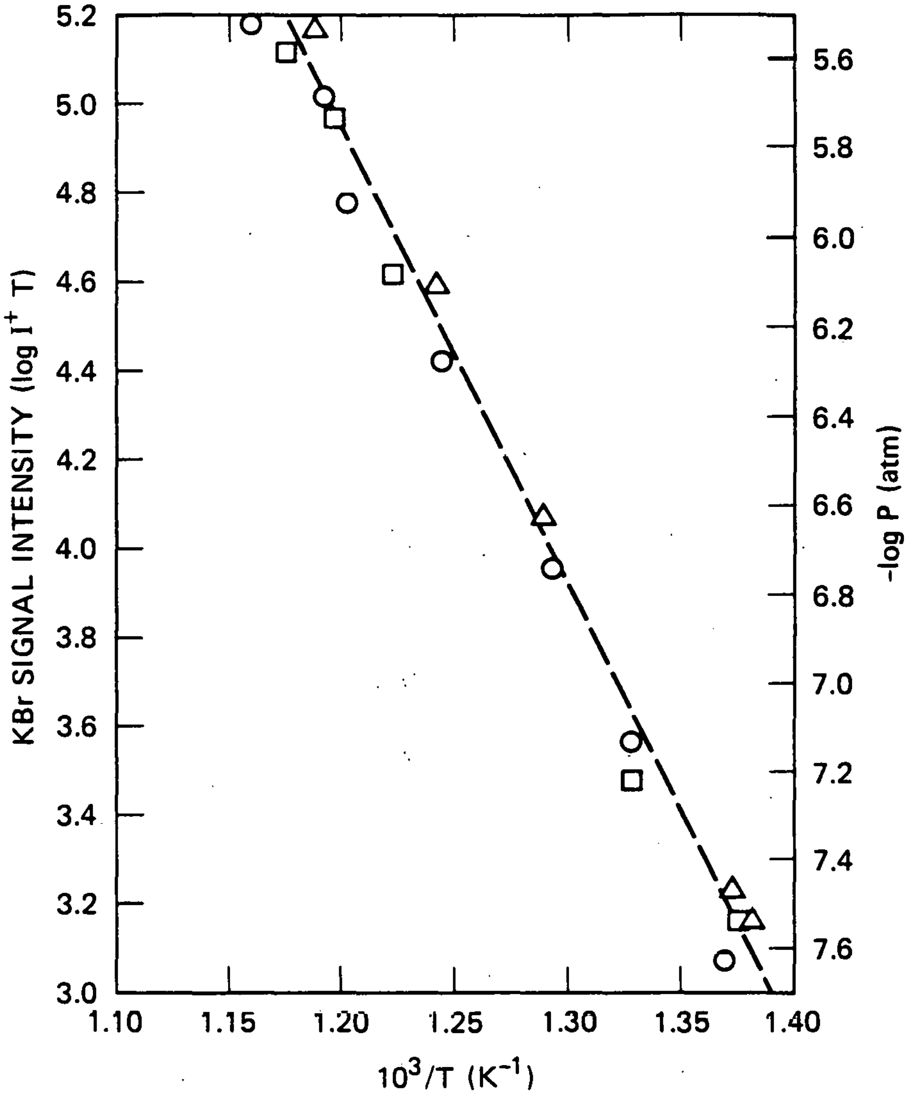

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FIGURE 3 KBr SIGNAL INTENSITY AS A FUNCTION OF INVERSE TEMPERATURE

— — —, KBr pressure from Ref. 4; ○, Pure KBr; △, KBr-impregnated Spheron-6; □, Mechanical mixture of KBr and Spheron-6.

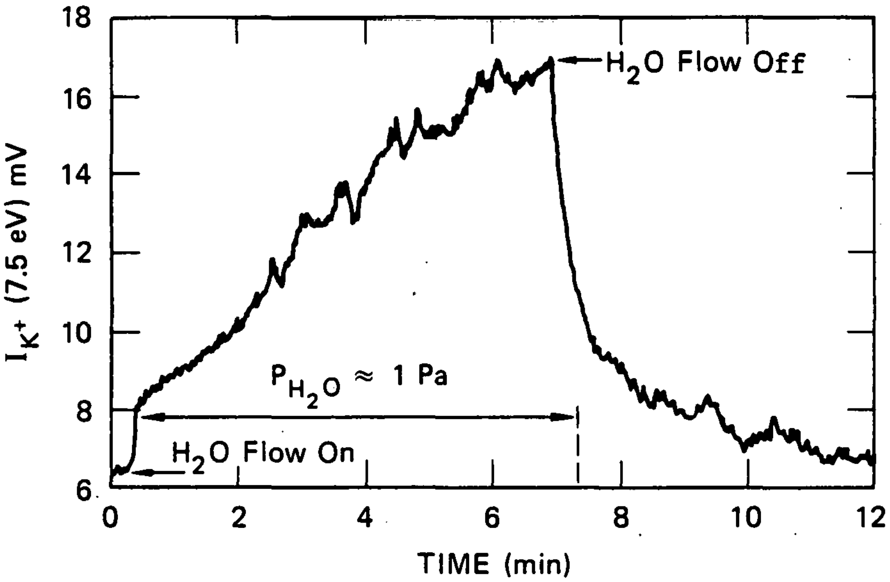

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FIGURE 4 EFFECT OF H_2O FLOW ON K^+ SIGNAL AT T = 985 K

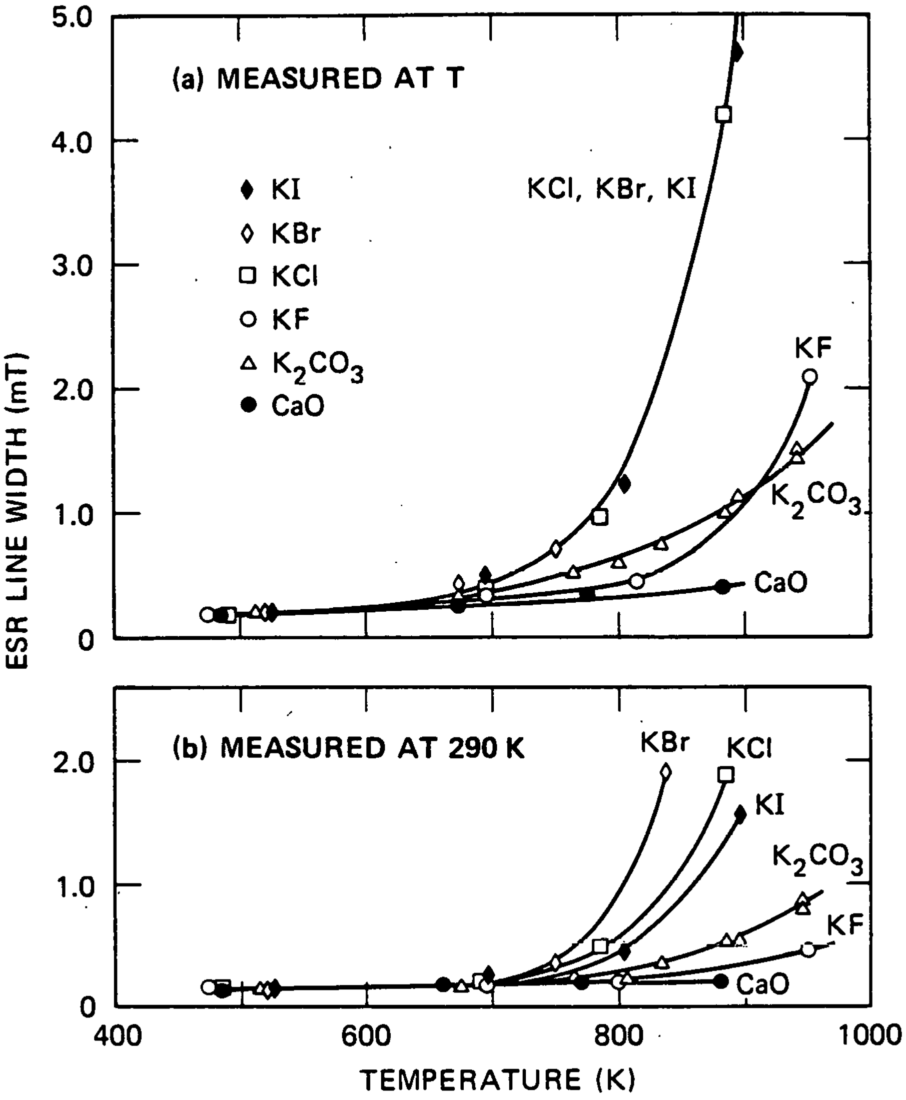

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FIGURE 5 EFFECT OF TEMPERATURE ON ESR LINE WIDTH OF CARBON-CATALYST MIXTURES
(C/Catalyst) = 0.03 g/g.

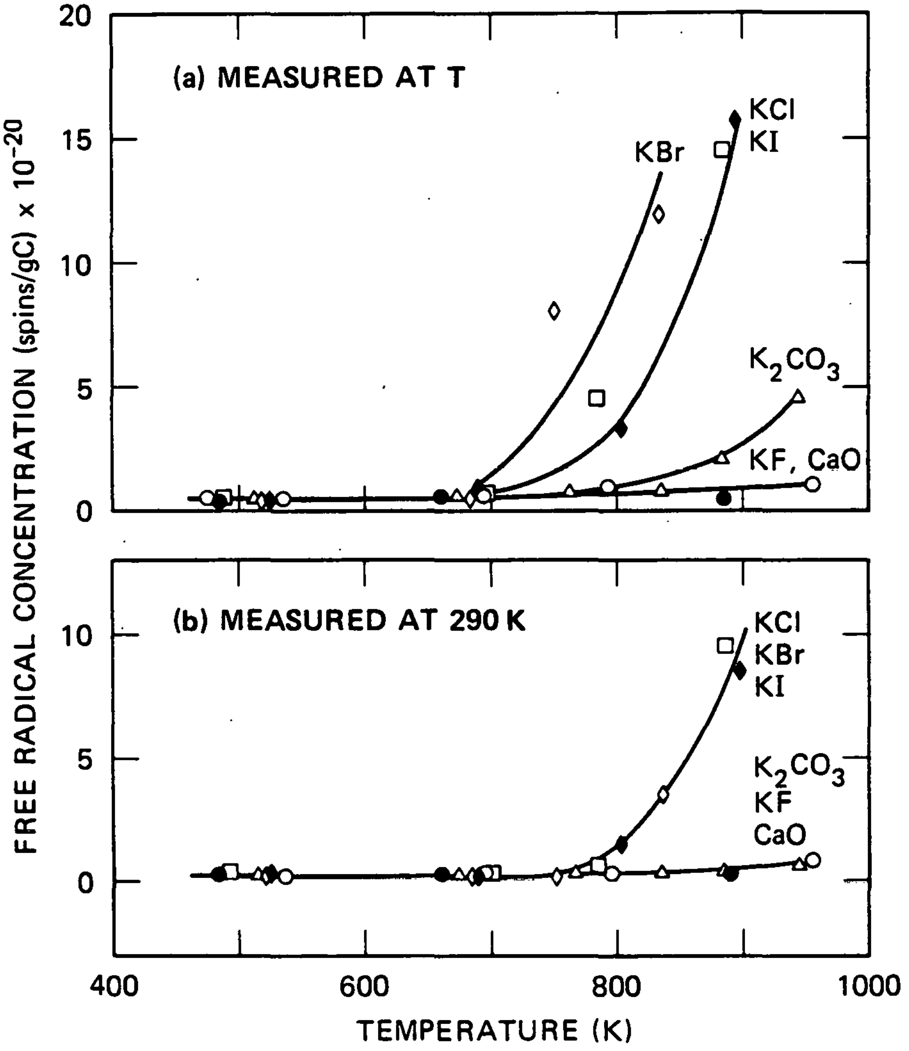

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FIGURE 6 EFFECT OF TEMPERATURE ON FREE RADICAL CONCENTRATIONS IN CARBON-CATALYST MIXTURES

(C/Catalyst) = 0.03 g/g; for symbols see Figure 5.

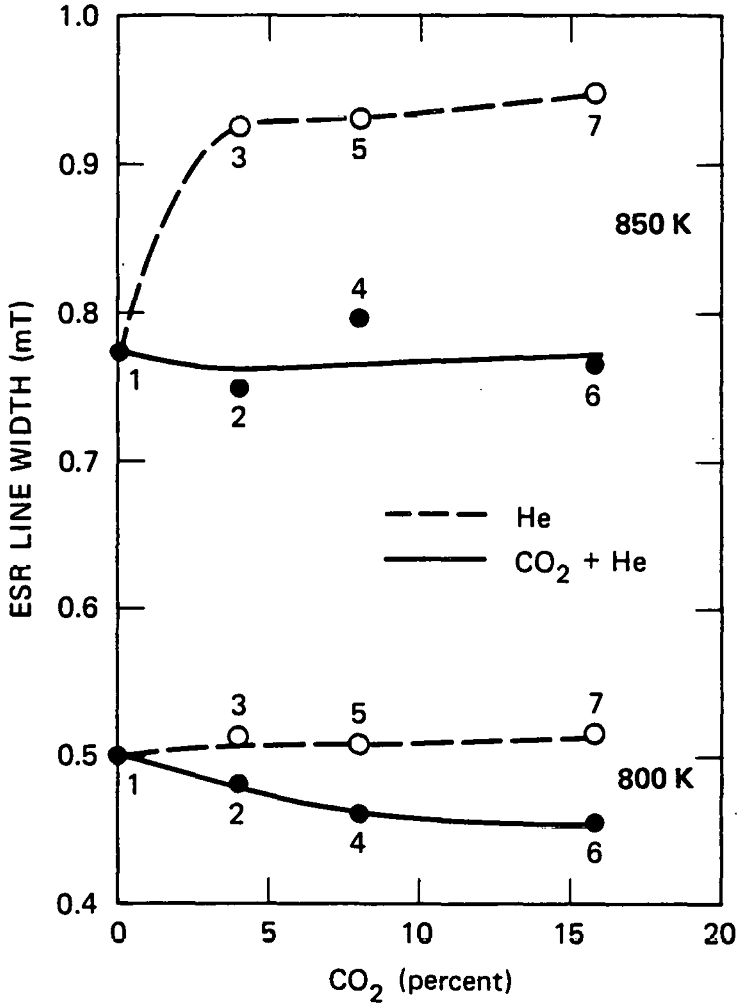

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FIGURE 7 EFFECT OF CO_2 ON ESR LINE WIDTH OF CARBON-CATALYST MIXTURES

(C/K_2CO_3) = 0.03 g/g. Numbers identify sequence of measurements.

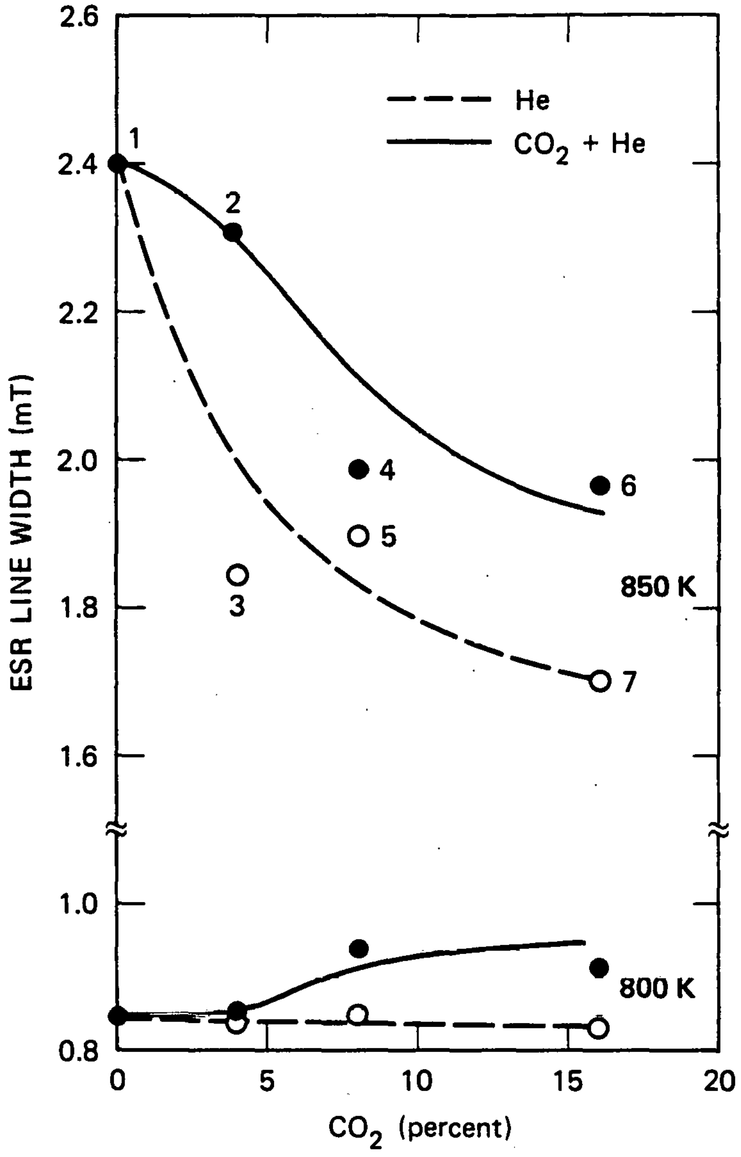

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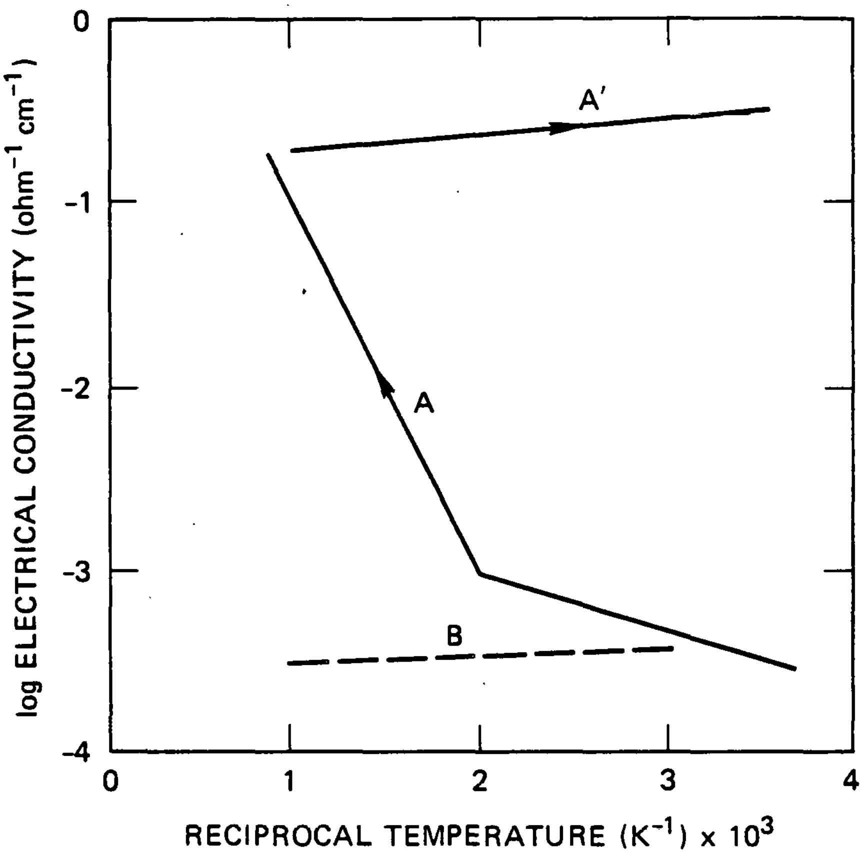
FIGURE 8 EFFECT OF CO_2 CONCENTRATION ON FREE RADICAL CONCENTRATIONS IN CARBON-CATALYST MIXTURES

(C/K_2CO_3) - 0.03 g/g. Numbers identify sequence of measurements.



JA-2202-47

FIGURE 9 ELECTRICAL CONDUCTIVITY OF ILLINOIS No. 6 COAL CHAR COMPRESSED WAFERS

Curves A and A': impregnated with K_2CO_3 (10 wt% K); Curve B: no additive.