Microwave-Specific Enhancement of the Carbon–Carbon Dioxide (Boudouard) Reaction

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Supporting Information

ABSTRACT: The Boudouard reaction, which is the reaction of carbon and carbon dioxide to produce carbon monoxide, represents a simple and straightforward method for the remediation of carbon dioxide in the environment through reduction: \( \text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2\text{CO} \). However, due to the large positive enthalpy, typically reported to be 172 kJ/mol under standard conditions at 298 K, the equilibrium does not favor CO production until temperatures >700 \(^\circ\)C, when the entropic term, \(-T\Delta S\), begins to dominate and the free energy becomes negative. We have found that, under microwave irradiation to selectively heat the carbon, dramatically different thermodynamics for the reaction are observed. During kinetic studies of the reaction under conditions of flowing CO2, the apparent activation energy dropped from 118.4 kJ/mol under conventional convective heating to 38.5 kJ/mol under microwave irradiation. From measurement of the equilibrium constants as a function of temperature, the enthalpy of the reaction dropped from 183.3 kJ/mol at \( \sim \)1100 K to 33.4 kJ/mol at the same temperature under microwave irradiation. This changes the position of the equilibrium so that the temperature at which CO becomes the major product drops from 643 \(^\circ\)C in the conventional thermal reaction to 213 \(^\circ\)C in the microwave. The observed reduction in the apparent enthalpy of the microwave driven reaction, compared to what is determined for the thermal reaction from standard heats of formation, can be thought of as arising from additional energy being put into the carbon by the microwaves, effectively increasing its apparent standard enthalpy. Mechanistically, it is hypothesized that the enhanced reactivity arises from the interaction of CO2 with the steady-state concentration of electron–hole pairs that are present at the surface of the carbon due to the space-charge mechanism, by which microwaves are known to heat carbon. Such a mechanism is unique to microwave-induced heating and, given the effect it has on the thermodynamics of the Boudouard reaction, suggests that its use may yield energy savings in driving the general class of gas–carbon reactions.

1. INTRODUCTION

The remediation of carbon dioxide emitted into the atmosphere, primarily from energy-generation combustion processes, is of considerable concern due to the profound contribution it makes to the processes of global warming. Although there are a number of proposed remediation schemes, including geoengineering (sequestration) and rapid carbonate formation, among the most appealing is the reduction of CO2 to more synthetically useful molecules. Unfortunately, this is extremely difficult to accomplish due to the high thermodynamic stability of CO2. Among the oldest and simplest methods to activate CO2 is its reaction with carbon to produce carbon monoxide (reaction 1).

\[
\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO} \quad \Delta H = 172 \text{ kJ/mol} \tag{1}
\]

This reaction, called the Boudouard reaction after its discoverer, has been known since 1905 and is one of the equilibria that takes place during the gasification of coal and other carbon-rich sources. The reaction is highly endothermic; as such, the equilibrium lies far to the left, with CO2 being the favored product. However, the free energy of the formation of CO2 is relatively insensitive to temperature, while the entropy is positive; at high temperatures (>700 \(^\circ\)C is typically cited), the free energy change becomes negative, making CO formation progressively more favored. For this reason, the reaction only plays a significant role in high-temperature (>900 \(^\circ\)C) gasification and smelting processes. The contemporary appeal of this reaction is that it potentially represents a means of CO2 remediation by converting it to more synthetically flexible CO. Its use has been proposed as part of “clean coal” schemes that convert the CO2 product gas to CO, which can then be used to produce hydrogen via the water–gas shift reaction or hydrocarbons through the Fischer–Tropsch process. In addition, there is a substantive synthetic chemistry whereby CO is utilized as a carbylation reagent. In short, while this reaction offers great potential for use in CO2 remediation and utilization schemes, the high temperatures at which it occurs efficiently tend to preclude many of these.

In this study, we report that the use of microwave radiation to drive the Boudouard reaction results in a dramatic change in the observed thermodynamics of the reaction, which pushes the equilibrium to the right, favoring the production of CO, at...
temperatures that are over 400 °C lower than can be achieved by conventional convective heating. To the best of our knowledge, a change in the apparent thermodynamics of a reaction due to the presence of microwave irradiation has not been previously reported. This work opens up the possibility that, through the use of microwaves, reactions that are thermodynamically unfavorable can be exploited at reasonable temperatures.

2. EXPERIMENTAL SECTION

Materials. The carbon source was steam activated charcoal (50–200 mesh) with a surface area of 992.3 m²/g, which was obtained from Fisher and used as received. Carbon dioxide (99.9999% purity) was obtained from Airgas and used as received. A detailed characterization of the carbon source is in section I of the Supporting Information.

Methods. Dielectric measurements were made on an Anritsu 37347E “Lightning E” Vector Network Analyzer. The Nicolson–Ross–Weir (NRW) algorithm is based on the inversion of the Fresnel–Airy formulas expressing the normal reflection and transmission coefficients of a material layer through the wave impedance of the medium and its refraction index. These values reveal complex permittivity and permeability. A detailed description of the dielectric instrumentation and measurements is in section IIa of the Supporting Information.

Microwave experiments were carried out in a CEM Discover commercial microwave system under conditions of fixed applied microwave power. To acquire flow (kinetic) and static (equilibrium) data, two reaction systems were designed and built to fit in the microwave cavity. In the flow system, the reactant gas passes up through the catalyst, which is positioned at the center of the microwave cavity. The reactant gas is introduced into the system using a calibrated mass-flow controller. The volume of the product gas stream as a function of time is then determined with a totalizing mass flow meter. The static system for determining the equilibrium constants, is a closed reaction vessel situated in the microwave cavity that allows introduction of the reactant gas into an evacuated cell containing carbon. In both systems, the internal pressure is constantly measured using a transducer, and the temperature of the catalyst surface is measured in situ using an external pyrometer that is focused on the surface through a germanium window. Both systems have a septum port that allows aliquots to be extracted and analyzed by gas chromatography. Details of the apparatus are given in section III of the Supporting Information.

Data Acquisition and Analysis. The penetration depth of the microwaves in the carbon at 2.45 GHz was calculated from the values of the real and imaginary dielectric constants taken from the dielectric measurement (Supporting Information section IIb).

Flow Experiments. Microwave. CO₂ flowed at a constant rate over the carbon sample, spread out on a quartz frit at the center of the microwave cavity. Using a fixed microwave power, the carbon is heated and the surface temperature measured with an IR pyrometer. The rate of gas evolution in vol/time and the total volume as a function of time are collected by a totalizing mass flow meter. Gas was extracted from the flowing system at 1 min intervals through a septum and analyzed by gas chromatography (gc) (Shincarbon column), which had been calibrated with standard samples of CO and CO₂ to determine the moles of both gas constituents in the reaction.

Thermal. For flow reactions carried out under thermal conditions, a reaction tube of the same diameter and having the same mass of carbon, spread out over a quartz frit, is brought up to the desired temperature in a Lindberg tube furnace packed with quartz wool to insulate the tube. After the system comes up to temperature, the flow of CO₂ commenced using the mass flow controller. As with microwave experiments, the volume of gas evolved during the reaction was measured using a totalizing mass flow meter. The product gas was sampled at the same 1 min intervals as in the microwave experiment and analyzed by gas chromatography to determine the composition.

Static Experiment. In the evacuated closed reaction cell, with carbon spread out across the bed and situated in the microwave cavity, a fixed volume of CO₂ is introduced with a gastight syringe. Microwave irradiation is initiated at a fixed power, and the system is allowed to come to equilibrium. Equilibrium is deemed attained when the temperature of the carbon and the pressure cease to change. Samples of the gas are then extracted and the molar composition determined. The partial pressures of the individual gases are determined from the total pressure of the system, which is measured using a transducer, and the mole fraction of the constituents determined through the gc analysis.

Full details of the flow and static experiments are in section III of the Supporting Information.

Data Analysis. Rate constants were determined from a linear regression fit of the steady-state region of the concentration versus time plot. For the microwave-driven experiment, this occurs after ~300 s—after the initial outgassing process is completed as described in the text and in section IV of the Supporting Information. For the thermal reaction, the entire curve is fit as any outgassing process takes place before the reactant is introduced.

Activation Energy. The activation energy was determined by a weighted least-squares fit of the natural log of the rate of CO production to the reciprocal of the temperature.

Statistical details of the regression analysis are in section V of the Supporting Information.

Van’t-Hoff Equation. The enthalpy (ΔH) was determined by a weighted least-squares fit of the natural log of the experimentally determined equilibrium constant versus the reciprocal of the temperature.

Thermochemical Calculations. For the thermal reaction, the thermodynamic parameters, specifically ΔH and ΔS, were calculated using standard thermodynamic tables. The enthalpy and entropy were corrected for temperature using the heat capacities of the reactants and products to better match the temperatures at which the microwave reaction was experimentally determined. The free energy and equilibrium constants were, in turn, computed from ΔH and ΔS using the standard thermodynamic relationships.

For full details of the thermochemical calculations, including all data used, see section VII of the Supporting Information.

3. RESULTS AND DISCUSSION

Microwave Absorption and Heating Processes. The volumetric heating of carbonaceous materials by microwave radiation at 2.45 GHz generally proceeds efficiently, depending on the type of carbon.Studies of dielectric relaxation processes in different kinds of carbon have indicated that heat is produced primarily through space-charge (interfacial) polarization, which is typical for solid dielectric materials. Qualitatively, this loss mechanism arises from charge carriers (electron–hole...
pairs) that become trapped at the surface in defect and impurity sites and grain boundaries.\textsuperscript{19} The trapping process impedes the charge recombination, thereby dephasing the charge transport from the oscillating electric field and resulting in dielectric loss. The loss process is measured through the imaginary part of the dielectric constant, $\varepsilon''$ (eq 2), with the magnitude of the loss often given through the loss tangent (eq 3).\textsuperscript{20}

$$\varepsilon = \varepsilon' - i\varepsilon'' \quad (2)$$

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (3)$$

The magnitude of the loss, and hence the degree of heating, varies among different types of carbon. Carbon activated at high temperature, for example, tends to heat extremely efficiently in the microwave. The results of measuring the real and imaginary components of the dielectric constant for our specific material are shown in Figure 1 (Supporting Information, I–II). There is a small maximum in the loss tangent (tan $\delta$) quite close to the excitation wavelength of the microwave oven, with the loss tangent having a value of 0.18 ($\pm$0.06) at 2.45 GHz. It is important to note, however, that the dielectric loss tends to increase as a function of temperature for activated charcoals.\textsuperscript{16}

From the values obtained for the components of the dielectric constant at 2.45 GHz, the attenuation factor for the microwaves propagating through the carbon was 20.42 m$^{-1}$, which yields a penetration depth, $D_p$, of 24.5 mm (Supporting Information, IIb). In the experiments carried out in the study, the diameters of the carbon samples used were 24 mm for the static and 11 mm for the flow experiments. Because the radiation comes in uniformly from all sides, we would not expect to see significant attenuation of temperature at the centers of the samples.

The actual uniformity of the microwave heating of the carbon under microwave irradiation was assessed using thermal imaging, collected while looking down the reaction tube directly at the surface of the carbon (1 g, 24 mm diameter) through a germanium window. Images were collected after 30 s of microwave irradiation at 75, 100, 125, and 150 W (Figure 1b). Consistent with volumetric heating of the sample, the surface of the carbon exhibits the highest temperature at the center, which decreases toward the edges of the cell, where convective heat transfer to the surroundings is greatest. While the temperature across the surface generally increases in going from the edge to the center, it is not completely uniform, with variations and hot spots observable in regions of the surface. Such heterogeneity, which is often transitory, is not uncommon for microwave heating of solids and can arise from a number of factors, including defect and impurity sites. In our studies, the temperature of the surface of the carbon was collected using an IR thermometer, which averages the temperature over a 13 mm area of the carbon. The presence of these transitory hot spots contributes to observed temperature fluctuations, even under steady-state conditions.

As discussed, the Boudouard reaction (reaction 1), because it is endothermic, requires high temperatures to drive the equilibrium substantially to the right and produce any significant amount of CO. Our hypothesis is that microwave heating of the carbon may result in a more facile generation of CO with much lower energy expenditure. The rationale for this arises from two properties unique to microwave heating. One is simply based on selective heating, by which the microwaves will selectively heat the carbon to the point where the reaction occurs without the necessity of heating the entire system. The second is the possibility of a microwave-specific enhancement due to the space-charge heating mechanism that is intrinsic to microwave heating of carbonaceous solids.

**Kinetic Studies.** The reaction under conditions of flowing CO$_2$ was carried out in a quartz reactor system (Supporting Information, section III), with activated carbon (0.5 g) spread out evenly across an 11 mm diameter quartz frit. The sample was positioned in the center of the microwave cavity, with CO$_2$ flowing up through the carbon at 50 mL/min via a mass flow controller. The volume of the gaseous reaction product was measured using a mass flow meter, with the molecular compositions determined through gas chromatographic (gc) analysis. Under these conditions, the internal pressure remained close to ambient through the duration of the run. For comparison purposes, the reaction was also carried out under conventional convective heating in a thermostatically controlled tube furnace, using identical conditions of sample size, mass, and reactant flow. Importantly, although we have endeavored to match as closely as possible the reaction conditions in the microwave and convective thermal reactor, in the convective thermal reactor, both the carbon and the gas phase reactant and product will always be at the same temperature, while, in the
microwave, the carbon surface will be at a significantly higher temperature than the gaseous medium. Finally, while both the microwave and convectively heated reactions are inherently thermal in nature, we distinguish between them in this report by referring to them as “microwave” and “thermal”, respectively.

The production of CO from the reaction of CO₂ with carbon under microwave and thermal conditions as a function of time is shown in Figure 2a and b, respectively. Under microwave irradiation (Figure 2a), we observe a rapid evolution of CO in the very early stages of irradiation; however, after approximately 300 s, the rate decreases and becomes constant, commensurate with the steady-state production of CO. The origin of the initial, rapid flux of product gas is due to adsorbed species that are present on the surface of the activated charcoal prior to initial heating. This was verified by measuring the microwave-induced gas evolution from the activated carbon under a flow of inert gas (Supporting Information, section IV). The species evolved include CO, CO₂, and H₂, which can come from the reaction of carbon with adsorbed CO₂, CO, and H₂O. The evolution of these species falls to negligible amounts (≤10⁻⁷ mol) after approximately 300 s under 75 W of irradiation (Figure S5, Supporting Information) and more quickly at higher powers.

The rate of CO production under microwave conditions, obtained from least-squares fitting of the linear, steady-state portion of the data, after the initial outgassing of adsorbed species, is quite reproducible over independent runs and increases systematically with increasing power/surface temperature (Table 1). At the highest power level, 150 W, we observed that the rate of CO production was almost unchanged from that at 125 W (1.56 vs 1.50 mmol/min, respectively) (Figure 2a). Analysis of the product distribution indicates that, at the highest power, virtually all of the CO₂ is consumed, suggesting that, at that power under this flow rate, the reaction is mass-limited. Increasing the flow of CO₂ to 75 mL/min in fact yielded an increase in the production of CO above the mass restrictions of the 50 mL/min flow rate. The higher flow rate yielded a rate of CO production of 1.66 mmol/min, which was consistent with the rate versus temperature trend observed for the lower power setting.

The production of CO under thermal conditions is shown in Figure 2b. As can be seen in Figure 2, product formation is quite linear with time. We do not observe the initial outgassing process that is observed in microwave heating because the carbon is brought up to the desired temperature under an inert atmosphere prior to flowing CO₂ over it. The rates of reaction obtained under thermal conditions are shown in Table 1. As would be expected, they increase steadily as a function of temperature. In addition, they are generally more reproducible over independent runs, as indicated by the small standard deviation of the rates compared to those of the microwave-driven reaction.

In comparing the two processes, it is clear that, over the range of temperatures studied, the microwave-driven reaction is faster than the equivalent thermal reaction. The difference between the microwave and thermal reaction is more pronounced at lower temperatures, where the microwave-driven reaction is over three times faster than the thermal reaction. The difference in rates decreases until, at the highest temperature used, the microwave rate is only 1.4 times faster than the thermal reaction. This behavior suggests that the two modes of driving the reaction must have fundamentally different temperature dependencies of their rate constants, which should be manifested in the Arrhenius parameters. Figure 3 shows Arrhenius plots for the thermal and microwave-driven reactions, based on the temperatures and rates given in Table 1. Good linear fits were obtained for both sets of data, from which the apparent activation energy for the microwave and thermal process was found to be 38.5 and 118.4 kJ/mol, respectively (Supporting Information, section V).

Table 1. Rate of CO Evolution under Microwave and Thermal Conditions

<table>
<thead>
<tr>
<th>Arhenius parameters</th>
<th>microwave</th>
<th>thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>applied power (W)</td>
<td>temperature (°C)</td>
<td>rate (mmol/min)</td>
</tr>
<tr>
<td>75</td>
<td>813</td>
<td>0.908 (±0.10)</td>
</tr>
<tr>
<td>100</td>
<td>912</td>
<td>1.32 (±0.04)</td>
</tr>
<tr>
<td>125</td>
<td>958</td>
<td>1.50 (±0.11)</td>
</tr>
<tr>
<td>150</td>
<td>992</td>
<td>1.66 (±0.07)</td>
</tr>
</tbody>
</table>

**75 ml/min flow rate.**
By equating the Arrhenius equations for the thermal and microwave process, \(1049^\circ C\) is found to be the temperature at which both processes generate CO at the same rate; above that temperature, the thermal process is more efficient, while, below it, the microwave process is more efficient. Clearly, the reaction under microwave conditions has a significantly lower apparent activation energy than it does under thermal conditions.

This suggests that the interaction of the microwaves with the carbon does more than just act as a source of selective heating; it in fact yields different energetics of the rate-determining processes occurring at the surface. Moreover, the pre-exponential factor for the microwave-driven reaction is significantly smaller, by 3 orders of magnitude, than it is for the thermal reaction. While we will not attempt to fully analyze the meaning of this difference, it is reasonable to suggest that, because the temperature of the gas in the microwave experiment is significantly lower than it is in the thermal experiment, it will have a smaller collision frequency with the surface, thereby contributing to the lower pre-exponential term.

The composition of the generated gas, measured as a function of time and temperature, was determined for both the microwave and thermal reactions (Figure 4a). Experimentally, for the microwave-driven reaction, the flow of CO began, and microwave power was applied. There is a slight induction period where CO increases relative to CO\(_2\) as the carbon is exposed to the microwave radiation. However, steady-state conditions appear to be attained at times greater than \(\sim 400\) s, depending on the applied power, with the amounts of CO and CO\(_2\) becoming relatively constant. The exception to this generalization is the 75 W experiments, which are less reproducible, as indicated by the larger standard deviation, and which show variation in CO and CO\(_2\) composition that deviated from steady-state conditions. Experiments run at 50 W of applied microwave power resulted in erratic CO production; reproducible kinetic data could not be attained. As such, 75 W of applied power in our system approximately represents a lower limit for the microwave-specific effect in our system. In the case of the thermal reaction (Figure 4a), the sample is already at temperature when the flow of CO\(_2\) commences, and no induction period is observed; the composition of gas is already established when the initial data point is collected at 60 s. For the thermal reaction, there is a slight decrease in the CO (and concomitant increase in CO\(_2\)) with time, the origin of which is not completely known. At the higher temperatures, steady-state conditions are ultimately attained by 600 s; however, at some of the lower temperatures, small decreases (<0.3%/min) in the CO are still evident. Thus, the values at 600 s should be viewed as an upper limit of the steady-state CO composition.

Consistent with the known thermodynamics of the reaction, the amount of CO produced increases with increasing temperature as the equilibrium is shifted to the right; this trend is observed in both the thermal and microwave processes. What is clear, however, when comparing the two modes of reaction (Figure 4b), is that, when steady-state conditions are reached, the microwave-driven reaction will tend to generate
more CO than is observed under thermal conditions at similar temperatures. As predicted from the Arrhenius equations for the two processes, we expect the rate of CO production to be greater in the microwave at lower temperatures, with the rates of the two processes converging as the temperature approaches 1049 °C. This trend can be seen quite clearly in the temperature-dependent composition data (Figure 5), where using the equilibrium expression \[ K_p = \frac{(P_{CO})^2}{P_{CO_2}} \] are shown in Table 2. The equilibrium constants for the thermal reaction as a function of temperature were reported previously.23 The reported values were obtained from the free energy change, \( \Delta G^\circ \), of the reaction as a function of temperature, calculated using the standard state heats of formation, \( \Delta H^\circ_p \), and standard entropies, \( S^\circ \), of the products and reactants at 298 K. To provide a quantitative comparison between the thermochemical properties of the microwave and thermal reaction, we have calculated the free energy change and the equilibrium constant using contemporary thermodynamic data (\( \Delta H^\circ_p \) and \( S^\circ \)). The data was temperature-corrected using the appropriate heat capacities to match the temperature of the carbon surface measured in the microwave experiments (Supporting Information, section VII).21

The difference in these thermodynamic quantities of the reaction can be seen in Table 2. It is clear from the data that the equilibrium constants for the microwave process are larger, so the \( \Delta G \) of the reaction is more negative than the thermal process at the lower end of the temperature range. The trend in the equilibrium constants of the two processes as a function of temperature is shown in Figure 7. Clearly, the microwave-driven reaction has significantly weaker temperature dependence than does the thermally driven reaction. Because the temperature dependence of \( K_p \) and \( \Delta G \) is dictated by the values of \( \Delta H \) and \( \Delta S \), there must be a significant difference in these quantities with the two methods of heating.

Because the enthalpy of the Boudouard reaction varies only slightly with temperature due to the small temperature-dependent heat capacities of CO and CO\(_2\), we can estimate the enthalpy of the microwave-driven reaction from a Van’t Hoff plot (\( \ln(K_p) \) vs \( 1/T \)).21 As can be seen in Figure 8, we obtain a good linear relationship for the regression analysis (Supporting Information, section V). The value of \( \Delta H \) obtained from the slope of the plot was 33.4 kJ/mol, and the value calculated for the thermal reaction was 183.3 kJ/mol (Table 2). Although both values were positive, consistent with the endothermic nature of the Boudouard reaction, the enthalpy change under microwave irradiation was approximately 5 times lower than that for the thermal reaction. Using the values obtained for the free energy and enthalpy, the

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Figure 5. The ratio of \( CO_{MW}/CO_{Th} \) in mmol, taken from the values in Figure 2, after 600 s.

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Figure 6. Values of temperature, pressure, and composition as a function of time as the system reaches equilibrium (1 g of carbon, 0.25 atm initial charge of CO\(_2\), 75 W irradiation).
Delta entropy change, $\Delta S$, was also determined (Table 2) and was significantly lower in the microwave-driven process.

Clearly, under microwave irradiation, the apparent thermodynamics of the reaction changes profoundly. The fact that the microwave-driven reaction has a negative $\Delta G$ at lower temperatures than the thermal reaction arises from its significantly lower value of $\Delta H$, as $\Delta H$ will be less than $-T\Delta S$ at lower temperatures. Conversely, the lower entropy means that, as the temperature increases, the thermal process will become more favorable much more quickly than the microwave process as $-T\Delta S_{\text{microwave}} > -T\Delta S_{\text{thermal}}$. When equating the thermodynamic relationship, $\Delta G = \Delta H - T\Delta S$, for the two processes, the temperature at which both processes have the same value for $\Delta G$ is 1164 K; above that temperature, the thermal process is more favorable for producing CO, and below it, the microwave process dominates.

Using thermodynamic relationships, the equilibrium constants can be determined over a wide range of temperatures for the two processes. From this, we can plot the predicted mole fraction of CO and CO$_2$ that will be present at a given temperature (Figure 9) (Supporting Information, section VIII). Significantly, on the basis of our thermodynamic calculations, the crossover temperature at which CO becomes the favored (i.e., $\Delta G < 0$) species occurs at 643 $^\circ$C in the thermal reaction and 213 $^\circ$C in the microwave reaction. Moreover, the temperature at which the desired CO product would account for >90% of the product is 419 $^\circ$C, while it is necessary to reach 763 $^\circ$C under conventional convective thermal heating. This suggests a rather pronounced advantage for the use of microwaves to drive this reaction. And in addition to the thermochemical effect, the heat required to run the reaction in the microwave is significantly less because it is not necessary to heat the entire system. Table 2 shows that the average temperature of the gas medium in our reactor system during the equilibrium measurements, estimated from the ideal gas law, is lower than the carbon surface by more than 800 $^\circ$C. With the microwave driven reaction, it is not necessary to heat the entire system, which suggests a large energy benefit to driving the reaction in that manner. Conversely, the lower temperature of the gas and its concomitant lower kinetic energy may affect how readily equilibrium conditions can be attained.

The data clearly shows that a microwave-specific effect exists and that it affects very fundamental aspects of the reaction. Although the origin of the effect has not been experimentally investigated, we should consider whether plasma formation plays a role in the process, as has been both suggested and actively utilized in prior studies of microwave applications for gas–carbon processes.24-25 Plasmas are relatively easily formed in the microwave, although typically not at the low powers

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Kp (microwave)</th>
<th>Kp (thermal)</th>
<th>$\Delta G$ (microwave) (kJ/mol)</th>
<th>$\Delta H$ (microwave) (kJ/mol)</th>
<th>$\Delta S$ (microwave) (J/mol)</th>
<th>$\Delta G$ (thermal) (kJ/mol)</th>
<th>$\Delta H$ (thermal) (kJ/mol)</th>
<th>$\Delta S$ (thermal) (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1086</td>
<td>267</td>
<td>68.3 (±10.6)</td>
<td>-38.1 (±1.3)</td>
<td>33.4 (±3.3)</td>
<td>65.6 (±3.1)</td>
<td>-27.7</td>
<td>183.3</td>
<td>194.3</td>
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<tr>
<td>1185</td>
<td>380</td>
<td>85.2 (±9.1)</td>
<td>-43.8 (±1.0)</td>
<td>-47.5 (±0.64)</td>
<td>-49.6 (±0.02)</td>
<td>-49.6</td>
<td>213.1</td>
<td>224.3</td>
</tr>
<tr>
<td>1232</td>
<td>390</td>
<td>103 (±6.66)</td>
<td>-56.1</td>
<td>-65.6</td>
<td>-76.3</td>
<td>33.4 (±3.3)</td>
<td>194.3</td>
<td>205.5</td>
</tr>
<tr>
<td>1265</td>
<td>404</td>
<td>111 (±0.17)</td>
<td>-62.5</td>
<td>-76.3</td>
<td>-83.5</td>
<td>-83.5</td>
<td>205.5</td>
<td>216.7</td>
</tr>
</tbody>
</table>

*Estimated using the ideal gas equation. Calculated from $\Delta G = -RT\ln K_p$, where R is the ideal gas constant. All tabulated thermodynamic quantities and equilibrium constants were calculated from standard thermochemical data (see the Supporting Information).
employed in our studies. To assess whether there was any evidence of plasma formation under our reaction conditions, we measured the UV–vis spectrum of the light emitted from the reacting system. The presence of a plasma will yield emission in the UV and visible regions of the spectrum, and we would expect a strong characteristic series of emission bands between 450 and 600 nm associated with the C2 Swan system that is present in both CO and CO2 plasmas (Supporting Information, section IX). No emission lines were observed in the UV–vis region of the spectrum over the power range employed in this study. In fact, the only spectral feature observed was the onset of the blackbody emission at the long wavelength edge of our spectral window. This observation suggests that plasma participation is unlikely, although we cannot fully rule out plasma formation deep in the pores of the activated carbon where radiation might be largely reabsorbed.

The approximate magnitude of the microwave-specific enhancement can be determined from thermodynamic consideration. The enthalpy of the reaction can be determined in the standard way from the standard enthalpies of the products and reactants at the reaction temperature, T (eqs 4 and 5). For the thermal reaction, this is the difference in the product and reactant, including the relevant stoichiometry factors (eq 4).

\[
\Delta H_{\text{thermal}} = 2(\Delta H^\circ_{\text{CO}}) - (\Delta H^\circ_C) - (\Delta H^\circ_{\text{CO}_2}) \tag{4}
\]

\[
\Delta H_{\text{microwave}} = 2(\Delta H^\circ_{\text{CO}}) - (\Delta H^\circ_C + \Delta H^\circ_{\text{MW}}) \tag{5}
\]

\[
\Delta H_{\text{thermal}} - \Delta H_{\text{microwave}} \approx (\Delta H^\circ_{\text{MW}})_C \tag{6}
\]

For the gas phase reactant and products, it is assumed that, even though the average temperature of the gas in the medium is much lower in the microwave experiment (Table 2), the temperature of the gas equilibrates rapidly with the carbon surface when the reaction takes place. As such, the enthalpies are the same in both processes. For the carbon, because it directly absorbs microwaves, the enthalpy can be written as the sum of the thermal enthalpy and the enthalpy due to the microwave-specific contribution (eq 5). The magnitude of the microwave-specific enthalpy is the difference between the thermal and microwave reaction enthalpy (eq 6), which for our system is 149.9 kJ/mol.

Figure 9. Mole fraction of CO (red line) and CO2 (blue line) as a function of temperature for the microwave (solid) and thermal (dashed) Boudouard reaction, predicted from the calculated equilibrium constants and assuming 1 atm of pressure (see the Supporting Information, section VIII).

Figure 10. Proposed mechanism of the microwave-specific effect on the Boudouard reactions.

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This thermodynamic quantity likely represents a change in the surface energy of the carbon brought about by the mechanism of microwave heating.\(^1\) It is reasonable to postulate that this effect arises from the space-charge mechanism, by which the microwave radiation heats the carbon.

In particular, the oscillating electric field vector of the incident radiation creates transient electron–hole pairs, the hindered recombination of which represents one of the primary loss processes that lead to heating.\(^1\)\(^,\)\(^19\) Under constant impact frequency of the CO\(_2\) at the surface. Once oxidized, the depend on the steady-state concentration of radicals and the cations, respectively. These species are likely to represent schematically (Figure 10).\(^23\)\(^,\)\(^28\) The rate-determining step is in the Boudouard reaction involves oxygen transfer to the surface, oxidizing one of the impurity sites. The initial step in the Boudouard reaction negatively takes to be the rupturing of the oxidized carbon site by Conner for substrates adsorbed on oxide surfaces.\(^32\)\(^,\)\(^33\)

To the best of our knowledge, this is the first time it has been demonstrated that the method of heating a heterogeneous reaction can yield different thermodynamic parameters for a reaction from those observed thermally. The existence of this microwave-specific effect has important implications for reaction chemistry. If the microwave effect is general for other important gas–carbon reactions, it suggests that profound energy conservation might be achieved. More generally, it suggests the possibility that microwave effects at other solid surfaces might provide energetic and mechanistic advantages to other catalytic reactions, as has recently been observed for methanol oxidation over magnetic metal oxides.\(^34\)

**CONCLUSION**

To the best of our knowledge, this is the first time it has been demonstrated that the method of heating a heterogeneous reaction can yield different thermodynamic parameters for a reaction from those observed thermally. The existence of this microwave-specific effect has important implications for reaction chemistry. If the microwave effect is general for other important gas–carbon reactions, it suggests that profound energy conservation might be achieved. More generally, it suggests the possibility that microwave effects at other solid surfaces might provide energetic and mechanistic advantages to other catalytic reactions, as has recently been observed for methanol oxidation over magnetic metal oxides.\(^34\)

**REFERENCES**


**ASSOCIATED CONTENT**

- **Supporting Information**
  - Information regarding experimental procedures, materials, methods and apparatus, dielectric measurements, data analysis, thermodynamic calculations, and UV–vis spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.