



Reaction rate coefficient of fullerene (C_{60}) consumption by soot

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Abstract

The reaction of fullerene molecules with soot was studied by contacting sublimed C_{60} fullerenes with commercially available carbon black particles at different temperatures in the range 1023–1273 K. Fullerene mass data collected both pre- and post-reaction were fit to a simple first-order kinetic model and yielded a temperature-dependent reaction rate expression. The calculated collision efficiency of the reaction is of the order 10^{-8} and the activation energy is ~ 9.8 kcal mol $^{-1}$, which would be consistent with a surface diffusion reaction or a heterogeneous reaction. Simple extrapolation of the observed rate to the conditions of a fullerene forming flame would give a consumption rate six orders of magnitude too small to account for the rate of fullerene consumption observed in the post-flame zone of a fullerene-forming benzene/oxygen/argon flame. Extrapolation of the reaction rate to flame conditions also shows that the rate of consumption calculated here is too small to account for observed oscillations in the fullerene concentration profile which can be related to changes in the relative rates of consumption and formation. Calculation of activation energies required for the extrapolation of rates observed here to match those observed in flames yields significantly larger values than those obtained in the present study and are so large as to suggest that mechanisms other than those studied here control fullerenes consumption in flames. Other mechanistic possibilities for the consumption of fullerenes in flames include reactions of fullerenes with other flame species and fullerene–soot reactions in which soot reactivity depends on soot reactions with other flame species.

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1. Introduction

Fullerenes are ball-shaped all-carbon molecules discovered in 1985 [1] in graphite vaporization under inert gas at low pressure. Fullerenes have many properties different from either diamond or graphite. Potential applications include high-temperature superconductors, sensors, catalysts, optical and electronic devices, polymer composites, high-energy fuels, biological and medical materials, and single-gate electron transistors. Other interesting classes of fullerene or curved layer carbon, as opposed to graphitic or planar-layer carbon, that can also be found in fullerene-producing systems are nanostructures with tubular, spheroidal, or other shapes and consisting of onion-like or nested closed shells [2–5] and soot particles with considerable curved layer content [6,7].

Fullerenes can also be found in premixed hydrocarbon flames under reduced-pressure and fuel-rich conditions. They were first detected in flames in ionic form by the Homann group [8,9] and later isolated in macroscopic quantities by Howard et al. [10–12]. Higher fullerenes [13], derivatives containing hydrogen and oxygen [14,15] and fullerene nanostructures [4,5,16] and soot [6,7] have also been detected in premixed flames. Similar structures have also all been detected in diffusion flames [17].

Some evidence from previous flame studies can be interpreted to mean that fullerenes might be consumed by reaction with soot material in situ. In premixed flames, Grieco et al. [18] observed a severe drop-off in the flame concentration of fullerenes at relatively long residence times in the post-flame zone of a sooting flame. The region of fullerene loss occurs within a region of continued soot production, suggesting that fullerenes might be consumed by soot. Similarly, Hebgen et al. [17] found that fullerene concentrations in diffusion flames peak at the stoichiometric surface of the flame just prior to the onset of

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significant soot formation. This observation can also be interpreted to mean that fullerene molecules might be consumed by soot material.

Other studies have drawn conclusions about fullerene consumption by soot that might appear to be conflicting or might be indicative of different behavior under different conditions. Mochida et al. [19,20] found that fullerenes are carbonized at temperatures in the range of 473–2673 K by heat treatment of fullerene-containing soot produced by graphitic carbon vaporization in an electric discharge. This result would be consistent with the occurrence of fullerene consumption reactions involving the soot. However, Fuller and Banhart [21] and Burden and Hutchinson [22] observed the formation of fullerene molecules from the electron irradiation of soot also produced in an electric discharge.

To determine the behavior of fullerene molecules in the presence of combustion-generated carbon particles pertinent to soot and to test the hypothesis that a consumption reaction occurs, fullerene molecules were exposed to a commercially-produced carbon black, used as a well-characterized soot surrogate, at temperatures pertinent to the post-flame zone of sooting flames. The resulting data were analyzed quantitatively to determine the rate coefficient of the observed fullerene–soot reaction. This rate coefficient was evaluated by comparing it to the theoretical upper limit from simple collision theory and it was used to help interpret previous evidence that fullerenes may be consumed by reaction with soot during combustion synthesis of fullerenes.

2. Experimental

The set-up for the heat-treatment experiments is shown in Fig. 1. The reactor consists of a quartz tube (17-mm I.D.) which contains a combustion boat with pure C_{60} fullerenes upstream from a quartz wool plug containing an approximately uniform distribution of carbon black. The fullerenes were 99.5% pure C_{60} from Hoechst. The carbon black, Regal 330, from Cabot, had an average particle diameter of 33 nm. The bulk density of carbon black in the plug of quartz wool in the reactor was 0.0083 g/cm^3 , so

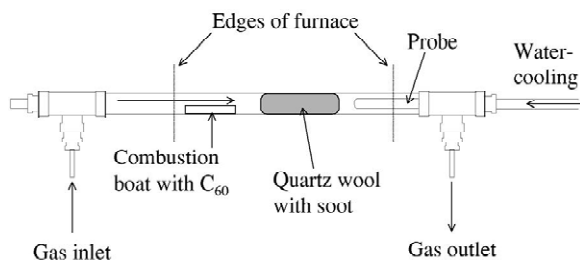


Fig. 1. Schematic of equipment for study of fullerene–soot reaction.

the specific surface area of the carbon black in the bed, SA_{soot} , was $7551 \text{ cm}^2/\text{cm}^3$. The porosity of the quartz wool with deposited carbon black in the quartz tube was 98% and a new bed was used for every experimental run. Commercial carbon black was used as a surrogate for lab-generated soot because its physical properties are well-characterized and it is commercially-available for reproduction or extension of the experiments. An experiment time of 9 min was used to ensure maximum C_{60} sublimation at all temperatures studied.

The quartz tube was positioned inside a 305 mm long \times 50 mm I.D. tubular furnace whose edges are indicated in the figure. Fullerenes sublime into the argon gas stream and are carried through the soot-laden quartz wool. The fullerenes react with the soot along the length of the bed and any unreacted fullerenes physically condense, and are collected, on the water-cooled glass probe.

The combustion boat was placed sufficiently upstream of the quartz wool to allow for radial diffusion of C_{60} prior to reaction. This arrangement ensured a uniform cross-sectional profile of C_{60} concentration at the beginning of the reaction zone. The temperature in the system was monitored with a thermocouple located inside and midway along the furnace, between the quartz tube and the furnace tube. The residence time of fullerenes inside the reaction bed was calculated as the ratio of the bed length to the argon gas velocity. The initial mass of fullerenes was measured gravimetrically while the post-reaction mass was determined by high-performance liquid chromatography (HPLC) applied to the deposited probe material. The HPLC system was operated with a Cosmosil Buckyprep column ($4.6 \times 250 \text{ mm}$ with 1.0-ml min^{-1} toluene flow) with a variable wave-length detector calibrated for C_{60} at a wavelength of 330 nm.

Prior to experimental runs, base case runs were performed with no quartz wool and with soot-free wool to determine the extent of C_{60} loss due to reactions other than those with the soot, none of which were observed. Additionally, it was observed that the sublimation of pure C_{60} resulted in a 20% residue of non-volatile material, consistent with previous studies [23]. The initial weight of the fullerenes in each subsequent run was corrected by this factor.

Experiments were run with a constant 4-s residence time at different constant furnace temperatures in the range of 1023–1273 K. The reaction bed length was 6.1 cm and the argon flow-rate for the different experiments was in the range $50\text{--}60 \text{ cm}^3 \text{ min}^{-1}$ (at 273 K and 1 atm).

3. Results

It is assumed that the gas flow through the reaction cell is plug-flow, thus allowing the bed length to be correlated directly to residence time. To obtain from the data a rate

coefficient for the reaction of fullerenes with soot, the following first-order reaction rate expression was used:

$$d[C_{60}]/dt = -k[C_{60}]SA_{\text{soot}} \quad (1)$$

where $[C_{60}]$ is the concentration of C_{60} , t is time, k is the rate coefficient, and SA_{soot} is the soot surface area per unit volume. To simplify the expression, it is also assumed that the fullerene–soot reaction is heterogenous with C_{60} being the limiting reactant and soot surface area constant. This allows the incorporation of the soot surface area into the rate constant, giving

$$d[C_{60}]/dt = -k'[C_{60}] \quad (2)$$

where $k' = kSA_{\text{soot}}$. Integration of Eq. (2) and writing the solution in terms of fullerene mass instead of concentration gives

$$\ln [M(C_{60})_0/M(C_{60})_f] = k't \quad (3)$$

where $M(C_{60})_0$ is the initial mass of fullerenes, $M(C_{60})_f$ is the mass of unreacted fullerenes collected downstream from the reactor, and t is the gas residence time in the reactor bed. Defining $k' = A \exp(-E_a/RT)$ and taking the natural log of both sides, the final rate expression is

$$\ln \ln [M(C_{60})_0/M(C_{60})_f] - \ln t = \ln A - E_a/RT \quad (4)$$

According to Eq. (4), a plot of the left side of the equation against $1/T$ should give a straight line with a slope of $-E_a/R$ and a y -intercept of $\ln A$.

A plot of the collected data is shown in Fig. 2. It can be seen that the data fall into a linear trend, thus allowing the parameters of the reaction rate coefficient to be calculated from the graph. Using the above value of SA_{soot} and

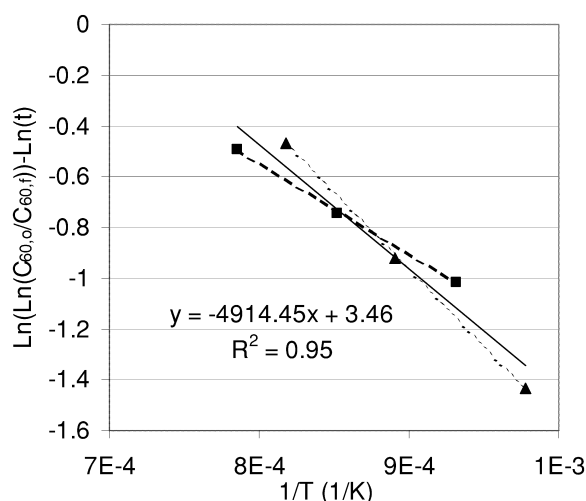


Fig. 2. Fullerene–soot reaction rate plot; day 1 data (■) with regression (long-dashed line), day 2 data (▲) with regression (short-dashed line), and full regression (solid line) with equation.

accounting for the scatter of the data with error limits of 1 S.D., the following expression for k is obtained:

$$k = 0.0042(\pm 0.0002) \exp[-4914(\pm 580)/T] \text{ cm s}^{-1} \quad (5)$$

The data in these experiments were collected over 2 different days and the daily data sets are represented individually in Fig. 2. It can be seen that data collected on the same day are perfectly collinear but the slopes of lines are somewhat different between the 2 days' data. The reason for this difference is unknown. Thus the two sets of data analyzed separately yield similar but not exactly the same kinetic rate coefficients. The parameters given in Fig. 2 are obtained from a regression of all the data together.

4. Discussion

Consistent with previous studies [17,18], the results from the plot shown in Fig. 2 indicate that fullerenes are indeed being consumed by soot and that the reaction is dependent on temperature in a manner that is consistent with first-order kinetics. It might be possible that the decline in fullerene mass is due in part to fragmentation of the fullerene molecules in addition to consumption by the soot. However, previous studies have shown that C_{60} is thermally stable in inert gas up to temperatures of 1720 K [24,25]. As the temperature in these experiments did not exceed 1300 K, it is unlikely that any unimolecular fragmentation occurred. Similarly, Whetten and Yerezian found that fragmentation of fullerenes due to surface collision, independent of the surface or temperature, required an unusually high impact energy [26]. This makes it unlikely that any collisional fragmentation of the fullerene molecules occurred. The exclusion of these two mechanisms leaves reaction with soot as the apparent mechanism for observed fullerene consumption.

In order to determine whether the fullerene–soot reaction observed in this experiment could explain the rates of fullerenes consumption previously observed in flames and tentatively attributed to a possible fullerene–soot reaction [18], the present data were used in the following analysis. From simple collision theory, the collision rate of C_{60} with the surface of soot particles is:

$$k_{\text{coll}} = [k_B T / (2\pi m)]^{1/2} [C_{60}] \quad (6)$$

where k_B is Boltzmann's constant and m is the mass of one molecule of C_{60} . If T is expressed in degrees K and $[C_{60}]$ in mol/cm^3 , Eq. (6) can be expressed as

$$k_{\text{coll}} = 135.5T^{1/2} [C_{60}] \text{ cm s}^{-1} \quad (7)$$

Using the collision rate as a basis for expressing the reaction rate and defining as γ the fraction of the collisions resulting in reactions, or collision efficiency, the reaction rate can be written

$$d[C_{60}]/dt = -k_{\text{coll}}\gamma SA_{\text{soot}} \quad (8)$$

Eliminating k_{coll} between Eqs. (7) and (8), we have

$$d[C_{60}]/dt = -135.5T^{1/2}[C_{60}]\gamma SA_{\text{soot}} \quad (9)$$

Comparison of Eqs. (1) and (9) reveals that

$$k = 135.5T^{1/2}\gamma \quad (10)$$

Eliminating k between Eqs. (5) (without the uncertainties) and (10) and solving for γ :

$$\gamma = 3.1 \times 10^{-5} T^{-1/2} \exp[-4914/T] \quad (11)$$

Collision efficiencies computed from Eq. (11) are less than unity as they should be and they rise with temperature, qualitatively as might be expected but with a magnitude that is very small at any temperature of interest. The efficiency is only 2×10^{-8} at the upper temperature limit of this experiment, i.e. 1273 K. This rate would be insignificant on the time scale of flame reactions. If the observed temperature dependence remained valid up to flame temperatures, the indicated collision efficiency would still be insignificant at flame temperatures, e.g. $\gamma = 6 \times 10^{-8}$ at 2000 K, as described below.

The measured collision efficiency was applied to fullerenes data from a premixed flame (pressure, 40 Torr; equivalence ratio, 2.4; cold gas velocity, 25 cm s^{-1} ; argon diluent, 10%) well-characterized in previous studies [18,27]. Soot particle size data obtained by McKinnon et al. [27] were utilized in conjunction with fullerene con-

centration, temperature, and soot mass concentration data from Grieco et al. [18] to see if the measured reaction rate could explain the rate of fullerenes consumption corresponding to an observed decline in fullerene concentration in the post-flame zone [18] which can be seen in Fig. 3. Although the soot particle size data only extend to 50 mm above the burner while the drop-off in fullerenes concentration is observed in the region of ~ 70 –80 mm, size information in the latter region was obtained by extrapolation. Soot surface area per unit volume of flame gases at different distances from the burner was computed from the profiles of soot mass concentration and particle size, taking into account approximately the reduction in surface area due to particle agglomeration using electron microscope images of the soot.

The consumption rates of C_{60} at different heights above the burner were computed using Eqs. (9) and (11) and the experimental temperature profiles [27]. The results are shown in Fig. 4. Although the validity of Eq. (11) and hence the accuracy of the calculation are unknown at temperatures above 1273 K and flame temperature varies from ~ 2000 to ~ 1350 K over the region 20–80 mm above the burner where the main fullerenes formation and consumption occur (Fig. 3), the results are nevertheless of interest for orientation. In the region of the fullerene concentration drop-off at 70–80 mm above the burner, the net rate of fullerenes C_{60} consumption calculated from the data in Fig. 3 is $\sim 2 \times 10^{-10} \text{ mol cm}^{-3} \text{ s}^{-1}$ which is a factor of 10^7 larger than the rate calculated for that region of the flame based on the data of this study (Fig. 4).

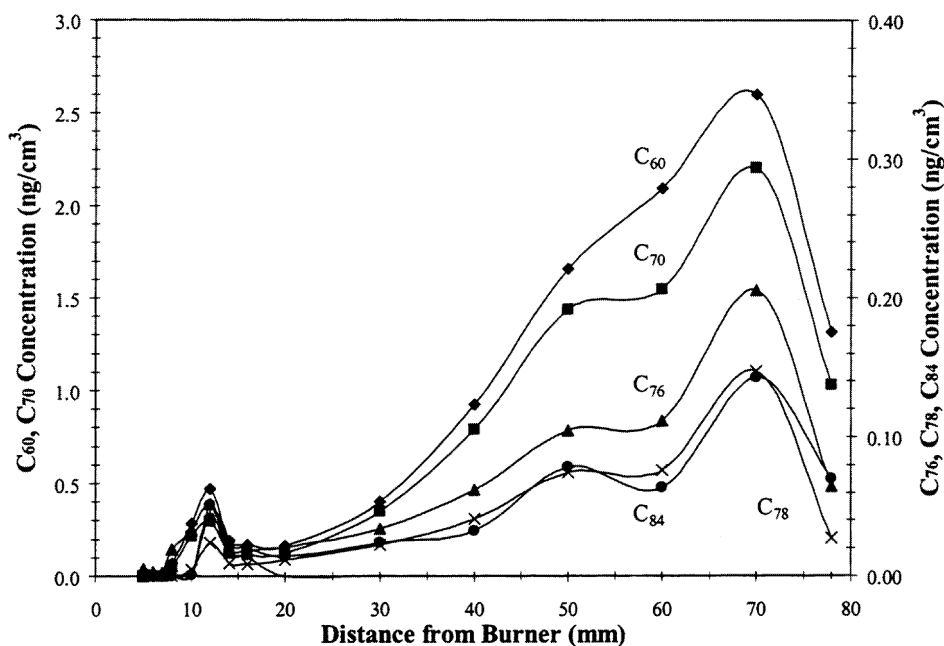


Fig. 3. Flame gas concentrations of fullerenes in a premixed benzene/oxygen/argon flame at different axial distances from the burner ($\phi = 2.4$, pressure 40 Torr, velocity 25 cm s^{-1} , argon dilution 10%) [18].

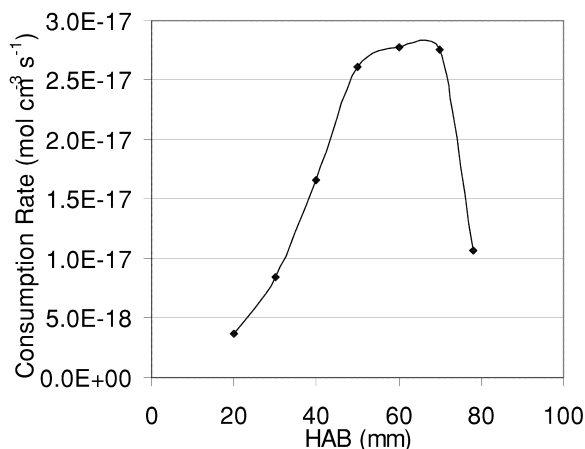


Fig. 4. Predicted consumption rate of fullerenes by soot in a premixed benzene/oxygen/argon flame ($\phi=2.4$, pressure 40 Torr, velocity 25 cm s^{-1} , argon dilution 10%).

Evidence for fullerenes consumption can also be seen earlier in the flame where fullerenes concentration is increasing in the region 20–70 mm above the burner. Although the net rate of fullerenes reaction in this region is clearly formation, it can be assumed that consumption reactions such as those that are clearly evidenced at 70–80 mm are also occurring in the earlier region where they compete with, and are overshadowed by, formation reactions. As shown by Kronholm and Howard [28] in the case of soot formation, analysis of the competition between formation and destruction can account for oscillations in the concentration profiles such as those seen for fullerenes in Fig. 3 in the region between about 40 and 70 mm above the burner. Accordingly, the net rate of fullerene formation is a relatively small difference between two large rates, i.e. the sum of all consumption reactions and the sum of all formation reactions. Subtle changes in either of these summed rates can result in significant changes in the net fullerenes reaction rate and account for the observed concentration oscillations. It can be calculated from the C_{60} concentration data in Fig. 3 that the increase in C_{60} consumption rate that would be required to explain the decreased net rate of formation between ~40 and ~60 mm above the burner, and hence to account for the oscillation in the C_{60} concentration profile in that region, is a factor of 2×10^6 larger than the consumption rate estimated for that region based on the present data.

Thus the fullerenes–soot reaction studied in this experiment is much too slow and its observed temperature dependence is much too small to allow the rates predicted for the flame to be of any significance in the region of major net fullerenes consumption or the earlier region of smaller changes in the net rates of fullerenes reaction. If a fullerenes–soot reaction were to be responsible for the fullerenes consumption rates in the flames, it would have

to be a mechanism whose rate increases by a factor of 10^6 or more in going from the conditions of the experiment to flame conditions. For example, calculations show that temperature dependence of the mechanism would have to be equivalent to an overall activation energy of $\sim 160 \text{ kcal mol}^{-1}$ to increase the rate of the fullerenes–soot reaction observed here to the incremental C_{60} consumption rate possibly reflected by the above-mentioned oscillation in the C_{60} concentration profile in the region 40–60 mm from the burner (Fig. 3) where the temperature is $\sim 1700 \text{ K}$. Similar calculations for the 70–80-mm region where C_{60} concentration drops (Fig. 3) and the temperature is $\sim 1380 \text{ K}$ show that the required overall temperature dependence would have to be the equivalent of a 490-kcal mol^{-1} activation energy to increase the fullerenes consumption rates observed in this experiment to that seen in the flame. The latter value is so large as to suggest that the mechanism of the fullerene–soot reaction studied in the present experiment would not play a significant role in the fullerenes consumption observed in the region of the large decrease of concentration.

The mechanism of fullerenes consumption by soot under the conditions of the present experiment has not been established. The magnitude of the observed activation energy, i.e. $E_a = 9.8 \text{ kcal mol}^{-1}$, would not be inconsistent with surface diffusion. Such a process might involve a reversible chemisorption of fullerene molecules on the soot with simultaneous surface diffusion to active sites where reactions with the soot material occurs. Given that the observed reaction rate is a minute fraction of the collision rate, e.g. $\gamma = 2 \times 10^{-8}$ at 1273 K , most of the fullerenes arriving at the soot surface would be either reflected or quickly desorbed according to this mechanism. An alternative explanation of the data might be a heterogeneous reaction between fullerenes and soot. In this interpretation, the observed activation energy would be the energy barrier for chemisorption, and this value along with the small magnitude of the observed collision efficiency would imply that a substantial fraction of the collisions have sufficient energy for reaction but that the probability of colliding at a suitable site in the soot structure is exceedingly low. In either mechanism, one might expect the population of radical centers or active sites in the soot structure to be important, and therefore the role of reactions between the soot and flame radicals could be important. Accordingly, one might expect the temperature dependence of the concentration of radicals, which can be the equivalent of overall activation energies of $\sim 50\text{--}70 \text{ kcal mol}^{-1}$ in fuel-rich flames of interest in fullerenes formation, to give rise to a higher temperature sensitivity than was observed in this work. Therefore, if the mechanisms being considered were to be important, the overall activation energy of the fullerenes–soot reaction would be expected to exceed substantially the value observed here. The possibility of such higher activation energies and possibly a higher reactivity of in situ flame soot as

compared to the collected carbon black used here might leave open the possibility of a significant role for the fullerenes–soot reaction in flames. Another possibility for explaining the observed consumption of fullerenes in flames is the reaction of fullerenes with other combustion intermediates and products such as polycyclic aromatic hydrocarbons, carbon monoxide, flame radicals, etc. Investigation of these different possibilities would provide interesting topics for further research.

5. Conclusions

Fullerene C₆₀ reacts with soot represented by a commercially available carbon black in the temperature range 1023–1273 K with the fullerenes being consumed in accordance with first-order kinetics. The collision efficiency of the reaction is very small, of the order 10⁻⁸ at the temperatures studied, and the activation energy is 9.8 kcal mol⁻¹. These characteristics would be consistent with reaction rate control by a surface diffusion controlled process or a heterogeneous reaction. Extrapolation of the observed consumption rates to flame temperatures using the observed activation energy would give a rate too small by a factor of 10⁶ to 10⁷ to explain the rate of fullerenes consumption observed in a fullerene-producing flame. The temperature dependence that would be required to allow the observed fullerenes–soot reaction when extrapolated to flame temperatures to be significant compared to observed rates in flames is so strong as to suggest that mechanisms other than those studied here must control fullerenes consumption in flames. Such other mechanisms may be reactions of fullerenes with other flame species and/or soot–fullerenes reactions with the reactivity of the soot dependent on soot reactions with other flame species, especially radicals.

Acknowledgements

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