Reaction of High-Velocity Atomic Oxygen with Carbon

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The rate of reaction of solid carbon with atomic oxygen impacting at a translational energy of approximately 100 kJ/mole has been measured at carbon surface temperatures ranging from 300-400 K. The magnitudes of the rates and the apparent activation energy (with respect to the carbon surface temperature) of approximately 15 kJ/mole are in good agreement with rates reported in the literature for the reaction of atomic oxygen with carbon at thermal impact energies. The relatively good agreement among these two sorts of laboratory measurements and reaction rates inferred from exposure of carbon to the low Earth orbit environment on various flights of the Space Shuttle suggests that there is little or no dependence of the rate of this reaction on the translational energy with which the atomic oxygen strikes the carbon surface.

Nomenclature

C' = rate of carbon loss in atoms/cm^2-s
%D = degree of dissociation of O_2 into 2 O atoms as defined by Eq. (5)
F_i = flux of species i in particles/cm^2-s, where $i = O, O_2$
$\Delta H°$ = heat of reaction in units of kJ/mole
I = intensity of incident light transmitted through target
I_0 = intensity of incident light
m_c = mass of a carbon atom, $\sim 2 \times 10^{-23}$ g
N_i = number density in units of particles/cm^3, where $i = O, O_2$
P = reaction probability for the O + C reaction
P_d = probability of dissociative electron-impact ionization
R = ratio of reaction probability of C with O_2 to that of C with O
S_i = mass spectrometer signal in amps, where $i = O, O_2$
T = absolute temperature of target, K
t = thickness of carbon removed by chemical reaction, cm
y = ratio of atomic to molecular oxygen in the mass spectrometer ionizer
η = ratio of S_O/S_{O_2} resulting from dissociative ionization of O_2
ϕ_O = fluence of atomic oxygen in atoms/cm^2
ρ = carbon density in g/cm^3
σ_i = electron impact ionization cross section, where $i = O, O_2$

Subscripts

c = crystalline form of element
g = gaseous form of element

Superscripts

$(\ )^*$ = translation excitation of 500 kJ/mole

Introduction

THE reaction of atomic oxygen with carbon,

$$C_c + O_g \rightarrow CO_g \quad \Delta H° = -357 \text{ kJ/mole} \tag{1}$$

has long been recognized as an important process both in combustion and reentry systems.[1-5] Recent observations of the removal of carbon from surfaces exposed to the atmosphere in low Earth orbit (LEO) on various flights of the Space Shuttle have renewed interest in the details of this reaction.[6-9]

A spacecraft in LEO, 200-700 km, experiences bombardment by an atmosphere whose predominant species is neutral, ground-state, atomic oxygen (see Fig. 1).[10] Although the ambient temperature is only of the order of 1000 K, the 8 km/s velocity of the spacecraft causes the oxygen atoms to strike the surface with a translational energy of 500 kJ/mole (5 eV). The atomic oxygen density at Shuttle altitude is approximately 10^9 atoms/cm^3, which results in an atomic oxygen flux of over 10^{14} atoms/cm^2-s. These conditions present a regime of gas-solid chemistry that has been the subject of very little investigation because of the difficulties inherent in reproducing them in the laboratory.

The existence of this significant, but poorly understood chemical regime leads to the question of whether increasing the translational energy of the oxygen atom increases the total rate at which carbon is removed from the surface. An attempt to extract a rate coefficient for the removal of a colloidal carbon coating included on the STS-3 Plasma Diagnostics Package (see below) suggested that such an enhancement might occur. The rate of a gas-solid reaction might reasonably be expected to be influenced by the translational energy of the gaseous atom if there exists a significant barrier to the adsorption of the atom onto the surface or if the reaction proceeds (to a significant degree) by way of a Rideal mechanism.[11]

Furthermore, although sputtering of carbon by atomic oxygen bombardment in LEO is not possible since the heat of formation of a gaseous carbon atom exceeds 700 kJ/mole, the high collision energy encountered on orbit does, at least in principle, open reaction channels other than reaction 1.[2] Two of these are

$$2C_c + O_g^* \rightarrow CO_g + C_g \quad \Delta H° = -125 \text{ kJ/mole} \tag{2}$$

and

$$3C_c + O_g^* \rightarrow CO_g + C_{2g} \quad \Delta H° = -9 \text{ kJ/mole} \tag{3}$$

Although such reactions are not intuitively likely, they are thermodynamically allowed.

This paper reports the results of an investigation of the rate of reaction of atomic oxygen with amorphous carbon at an impact energy of approximately 100 kJ/mole (1 eV) over a range of carbon surface temperatures of 300-400 K.

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Experimental

The apparatus used in this work was designed for the investigation of energetic oxygen atom surface chemistry. It consists of a three-chamber differentially pumped (oil diffusion pumps) vacuum system (see Fig. 2). The oxygen atom beam source is attached to chamber 1, which provides differential pumping for the source. Chamber 2 contains the sample target. Chamber 3 contains the quadrupole mass spectrometer detector.

An important part of the assembly of this facility was the development and testing of the oxygen atom beam source. The source is a modified, commercially available plasma torch. A schematic of the arc source is shown in Fig. 3. The modifications include attachments for a water-cooled nozzle, through which the atomic beam expands into the vacuum system, and exhaust channels to dispose of excess torch gas. The torch operates in the nontransferred mode, i.e., the electric arc is confined within the torch. A plasma is formed in helium by a dc arc. A small amount of O_2 ($\sim 2\%$ of the total gas flow) is injected downstream of the arc into the gas flow, where it is thermally dissociated into oxygen atoms by the hot helium. The high temperature and the isentropic expansion provide for the oxygen atom velocity, which results in a supersonic beam. A similar source has been described in the literature.[13]

Beam composition ($He/O_2/O$) and intensity were measured by a quadrupole mass spectrometer. The fractional dissociation of O_2 in the beam was calculated from relative mass spectral peak signals by the formula of Miller and Patch[14]

$$y = \frac{N_O}{N_{O_2}} = P_d\left(\frac{\sigma_{O_2}}{\sigma_O}\right)\left(\frac{1}{\eta}\frac{S_O}{S_{O_2}} - 1\right) \tag{4}$$

The percent dissociation is given by

$$\%D = 100y/(y+2) \tag{5}$$

The percent dissociation of O_2 in the beam was ~ 25 for all but one of the measurements reported here.

To convert an observed rate of carbon removal to an absolute reaction probability, it was necessary to measure the absolute flux (O atoms/cm^2-s) of the beam. This was accomplished by calibrating the response of the mass spectrometer to molecular oxygen. A nearly effusive, room-temperature beam source, for which it was possible to calculate reliably the flux and velocity distribution, was used for this calibration.[15] Comparison of the mass spectrometer signals obtained using this source with those obtained by adding to the mass spectrometer chamber a static pressure of O_2, measured by a Bayard-Alpert ionization gage, provided a means for rapidly recalibrating the mass spectrometer to O_2 before each experimental run.[16]

Since a mass spectrometer equipped with an electron impact ionization source is a number density detector, this calibration allowed the conversion of an observed mass spectrometer signal for O_2 in the beam to an absolute effective number density or "beam pressure." Beam number density was converted to flux by multiplying it by the nominal beam velocity of 3.5 km/s, which was measured by time-of-flight. The atomic oxygen flux was then obtained by multiplying the calculated O_2 flux by the fractional abundance of the O in the beam [see Eq. (4)]. Typical O atom fluxes were on the order of 10^{15}-10^{16} atoms/cm^2-s at the target.

Targets used in these experiments were amorphous carbon films ~ 300 Å thick deposited on fused silica disks. The sample was mounted in a liquid-nitrogen-cooled shroud to minimize contamination of the sample. Measurements were made to determine the effect of target surface temperature on the oxidation rate. Target temperatures ranged from 296-393 K.

Table 1 lists the fractional dissociation of oxygen in the beam (as $\%D$) and the oxygen atom flux at the carbon target for each of the carbon target surface temperatures used.

The reaction was monitored in situ by measuring the change in absorbance, and hence, thickness of the carbon film target as a function of O atom beam exposure time. The light produced by the arc in the beam source was used as the incident light source. A photomultiplier tube equipped with a near uv (250-400 nm) bandpass filter served as the detector. The rate of absorbance change was then converted to a reaction probability, defined as the probability that the impact of

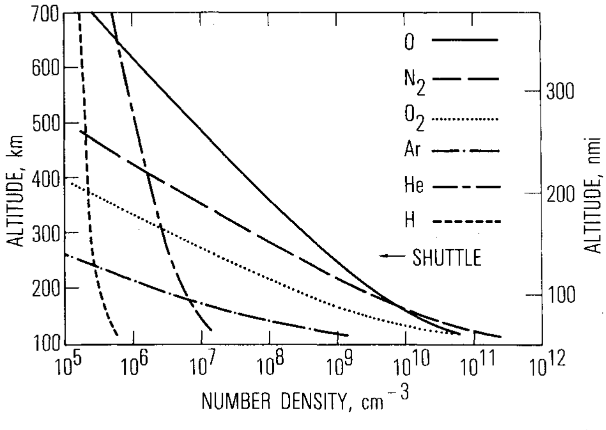

Fig. 1 Composition of the atmosphere in low Earth orbit (the theromosphere).

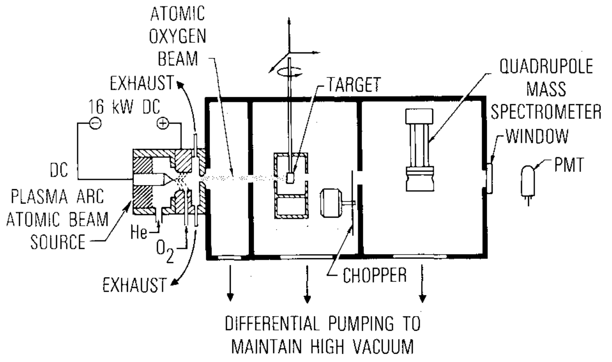

Fig. 2 High-energy oxygen atom surface chemistry apparatus.

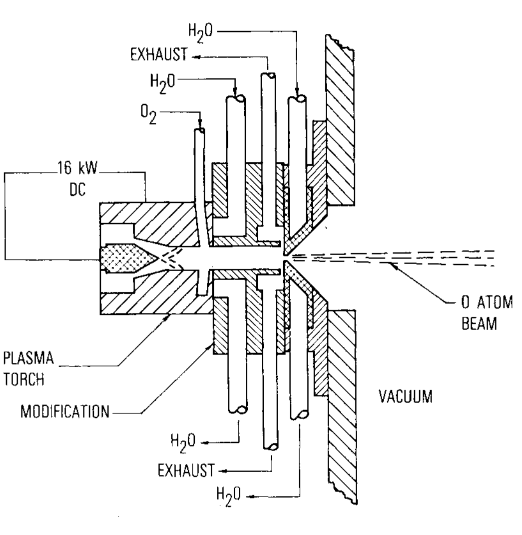

Fig. 3 Schematic illustration of the dc arc-heated atomic oxygen beam source.

an oxygen atom will remove a carbon atom from the surface, regardless of its final chemical state of aggregation.

The raw data of absorbance vs time were fit to a straight line by the method of least squares. The slope obtained was taken to be proportional to the total rate of disappearance of carbon C'. The proportionality constant was obtained by measuring the absorbance for a film whose thickness had been measured by ion sputtering monitored with secondary ion mass spectroscopy. Detailed calculations of the absorbance of thin carbon films on quartz substrates, taking into account the effects of optical interference between the film and the substrate,[17] using realistic values for the near ultraviolet index of refraction and extinction coefficient of carbon,[18] showed that this simplified fitting process underestimates the disappearance rate by about 25% owing to nonlinearity of absorbance vs thickness curves for films of less than ~100 Å. This factor was taken into account in the data analysis.

Results

Figure 4 shows the results of two experimental runs in which the carbon sample temperature was maintained at 296 K. The solid circles show the absorbance ($-\log_{10} I/I_0$) of the carbon film as a function of beam exposure time in ks, where the beam consists of $He/O_2/O$ (solid circles) and where the beam consisted of only He (open circles). The pure helium measurement was made to demonstrate that the change in absorbance was due to oxygen and not to any helium species or uv light in the beam. This was necessary because the reacting beam ($He/O_2/O$) was composed of ~98% He.

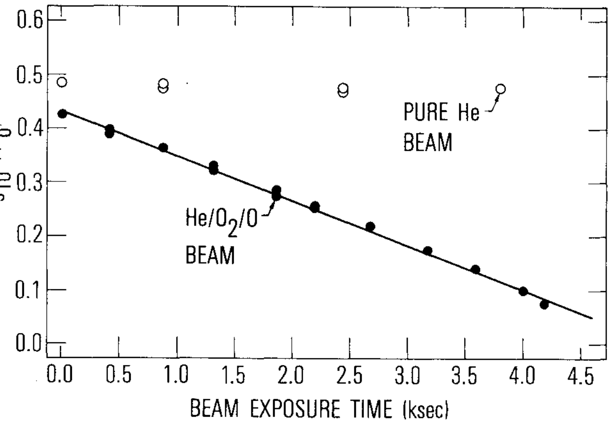

Fig. 4 Typical raw data of absorbance ($-\log_{10} I/I_0$) as a function of beam exposure time for beams of pure helium and $He/O_2/O$.

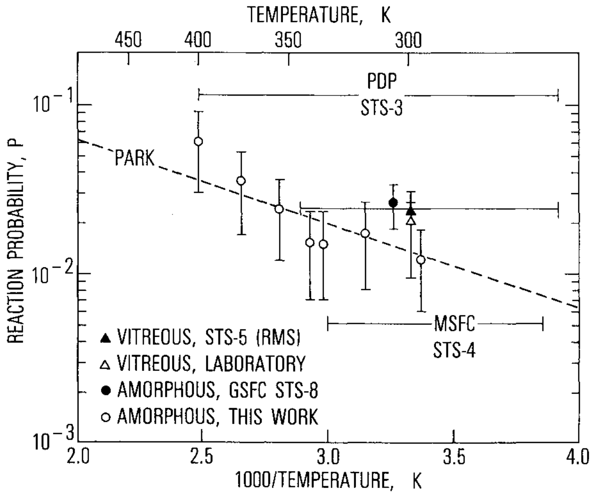

Fig. 5 Arrhenius plot of the reaction probability of the O + carbon reaction; see text for details.

The reaction probability for atomic oxygen is given by

$$P = C' [F_O + (R^* F_{O_2})]^{-1} \qquad (6)$$

Although both O_2 and O are present in the beam, it is believed that the reaction of carbon with O_2 is negligible at room temperature and the other temperatures studied here. Certainly this is the case for O_2 striking the surface at thermal velocities.[1] Furthermore, even at much higher carbon surface temperatures (>3X) than used in these experiments, the literature[2-4] indicates that the reaction with atomic oxygen dominates the molecular oxygen reaction by more than a factor of ~10. Values of the reaction probability for $R = 0$ calculated for each of the carbon target surface temperatures used are given in Table 2. The uncertainty in the reaction probability is set as ±50%. This uncertainty stems primarily from the precision to which the absolute beam flux is known. Note that even in the unlikely event the reaction probability of O_2 was as much as a tenth of the atomic oxygen reaction, the values of reaction probability calculated for oxygen atoms do not vary greatly from the $R = 0$ values, and are all within the experimental uncertainty assigned to these values.

Figure 5 shows an Arrhenius plot of the results (the data points are indicated as open circles). Fitting these data to an Arrhenius expression produces the equation

$$P = 4.2 e^{-1800/T} \qquad (7)$$

which implies an activation energy with respect to the carbon surface temperature of 15 kJ/mole.

Discussion

Figure 5 also shows several other data on the reaction of atomic oxygen with carbon including both thermal energy laboratory results and analyses of spaceflight results.

The line labeled "Park" is the equation

$$P = 0.63 e^{-1160/T} \qquad (8)$$

which Park used to describe the results of six different investigations of the oxidation of various graphitic materials for surface temperature ranging roughly from 300 to 4000 K.[1] A

Table 1 Experimental conditions

T_{carbon}, K	%D	F_O^{target} 10^{15}O atoms/cm^2-s
296	23	5.2
316	23	6.1
334	23	5.8
340	26	6.2
355	25	6.3
375	27	6.8
393	44	10.5

Table 2 Measured reaction probabilities for the O + C reaction

T_{carbon}, K	$P(R=0)$, 10^{-2}
296	1.2±0.6
316	1.7±0.9
334	1.5±0.8
340	1.5±0.8
355	2.4±1.2
375	3.5±1.8
393	6.0±3.0

variety of experimental techniques including discharge flow and thermal velocity atomic beams were used to prepare the atomic oxygen for the studies Park summarized. Park's fit produces an activation energy of ~10 kJ/mole, which is somewhat lower than the result obtained here. Indeed the low-temperature data of Marsh et al.,[5] which are included in Park's summary, suggest a higher activation energy than the composite fit. However, the precision of these various data is not sufficient to support the notion that these differences are statistically significant.

The remaining data in Fig. 1 include analyses of several observations of erosion of a variety of carbon surfaces, which were flown on the Space Shuttle. Approximate reaction probabilities have been calculated by

$$P=\frac{t\rho}{m_c\phi_O} \tag{9}$$

On the third flight of the Space Shuttle (STS-3), a colloidal graphite coating on a portion of the University of Iowa Plasma Diagnostics Package[19] (PDP) was completely removed.[7] It was estimated that the initial thickness of this coating was approximately 3 μm. The fluence of atomic oxygen received by this surface is not known. However, it has been calculated[20] that surfaces exposed in the bay on STS-3 received a fluence of 2.16×10^{20} cm^{-2}. Since the PDP spent a period of time outside the shuttle bay on the remote manipulator arm, the actual fluence it received was certainly greater than that received by surfaces in the bay. Thus, one may use the bay fluence value and a ρ of 2 g/cm^{-3} to calculate an upper limit of ~0.11 for P. The temperature history of the PDP is not known; however, simple heat balance considerations lead one to conclude that the carbon temperature could not significantly exceed 400 K, even in full sunlight. This datum is labeled "PDP, STS-3."

The STS-4 passive sample array (PSA) included a thin carbon film "10-30 nm thick."[6] This film was completely removed during the course of the flight. It has been estimated[20] that PSA received an oxygen atom fluence of 6.45×10^{19} cm^{-2}. Using the 30-nm thickness value and $\rho=2$ g/cm^{-3}, one calculates a lower limit of $\sim5\times10^{-3}$ for P. The temperature range for this sample was 260-330 K throughout the mission. This datum is labeled "MSFC, STS-4."

The STS-5 Evaluation of Oxygen Interaction with Materials Experiment (EOIM)[20] contained a sample of glassy carbon. The unprotected area of the carbon disk was visibly roughened after exposure to the orbital atmosphere. Laser interferometry was used to measure the extent to which the carbon was eroded. The peak-to-valley depth of the eroded area was 1.09 μm with a root-mean-squared depth of 0.3 μm.[8] The density of this sample[8] was 1.538 g/cm^{-3}. Using the fluence of atomic oxygen incident on the STS-5 EOIM experiment[20] of $9.9\pm3.0\times10^{19}$ O atoms/cm^2, one calculates an rms reaction probability of $2.3\pm0.7\times10^{-2}$. The temperature of the vitreous carbon sample was neither controlled nor monitored on the STS-5 experiment; however, the experiment tray did not exceed 350 K during the course of the flight.[21] This datum is shown as "Vitreous STS-5 (RMS)" in Fig. 5.

A sample of vitreous carbon identical to the one flown on STS-5 was exposed to the He/O/O$_2$ beam under conditions similar to those in the experiments reported here.[22] The reaction probability inferred from that experiment was $2.1\pm1.1\times10^{-2}$. This datum is shown in Fig. 5 as "Vitreous carbon, laboratory."

Not shown on Fig. 5 are the data of Gregory and Peters obtained from the STS-8 EOIM passive sample array. They obtain an Arrhenius expression of

$$p=1.0e^{-600/T} \tag{10}$$

for a vitreous carbon.[23] These are higher reaction probabilities and a lower activation energy than any of the other laboratory or flight data described above. These discrepancies may result from differences among the various materials. Marsh et al. report significantly different reaction probabilities and activation energies for the reaction of thermal atomic oxygen with Ticonderoga graphite crystals and paracrystalline porous carbon prepared by thermal decomposition of polyvinylidene chloride.[5]

On STS-8 the NASA/GSFC contamination monitor package (CMP) was flown as a getaway special experiment.[9] A temperature-controlled quartz crystal microbalance (TQCM) coated with 240 nm of amorphous carbon ($\rho=2$ g/cm^{-3}) was mounted on the CMP facing out of the payload bay. The temperature of the TQCM was maintained at 308 K. During periods when the TQCM was not directly illuminated by the sun, the mass loss rate ranged from $6\text{-}8\times10^{13}$ carbon atoms/cm^2-s. Taking into account variations in the atomic oxygen density on the flight,[24] one obtains a reaction probability of $2.6\pm0.5\times10^{-2}$. This uncertainty range accounts only for the quoted uncertainty of ±20% in the modeled O atom density.[10] This datum is labeled "Amorphous STS-8" in Fig. 5.

Conclusions

From the observations made and results presented in this paper, it can be concluded that the rate of the reaction of atomic oxygen with carbon, at collision energies of up to 96.5 kJ/mole (1.0 eV), does not depend strongly on the translational energy of impact. Indeed, when one compares laboratory and flight data for similar samples of carbon, the evidence that the reaction rates occurring on orbit are significantly different from the thermal rate of reaction of O atoms with carbon is not strong. However, the results of Gregory and Peters militate against drawing an unambiguous conclusion in this matter.

One practical significance of this result is that a temperature-controlled, well-characterized carbon surface can provide a useful bench mark for comparing the rates of oxidation of other materials in the LEO environment. Carbon has been proposed as a sensor for atomic oxygen on the Long Duration Exposure Facility.[6] The results of this investigation indicate that a quantitative measurement of the flux of atomic oxygen striking a spacecraft surface, independent of impact velocity, can be obtained from an in situ measurement of the rate of removal of carbon of known morphology.

Acknowledgments

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