Translational Energy Dependence of the Reaction of Atomic Oxygen with Polyimide Films

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Atomic beam experiments are reported in which atomic oxygen, produced in a conventional microwave discharge beam source, struck Kapton samples at a translational energy of approximately 0.14 eV. After being exposed to an atomic oxygen fluence in excess of 2×10^{19} cm^{-2}, the Kapton samples showed no evidence of reaction, either to the naked eye or under microscopic examination. These experiments, and others performed in this laboratory and elsewhere, strongly support the notion that there is a true dynamic barrier (in incident translational energy) of between 0.2 and 1 eV for the etching of polyimide films by atomic oxygen.

Introduction

THE work reported in this paper was undertaken in an attempt to answer more clearly the question of whether the rate of reaction of atomic oxygen with polyimide films depends, for energies up to 5 eV, on the translational energy of the atom. This section presents the background and motivation for this work. The second section of this paper describes the experimental apparatus and procedure. The final section presents the results and a discussion of their implications.

It has become well known that ambient atomic oxygen reacts with many organic materials at rates sufficient to cause significant erosion of the surfaces of spacecraft in low Earth orbit (LEO) during the course of typical satellite missions.[1-6] The effect of ambient oxygen on the polyimide Kapton§ has been particularly well documented.[1-3,7,8] Although the reaction of atomic oxygen with polymers has been reported in the literature,[7] the rates at which polymers and paints are removed in LEO is surprisingly high.[1,8] The origin of this discrepancy between erosion rates observed in LEO and those that might be inferred from the mass loss data of Hansen et al.,[7] who exposed a variety of polymers to essentially room temperature atomic oxygen, has not been conclusively identified.

It has been suggested that the rate at which an organic material is eroded in LEO is accelerated by the fact that atomic oxygen strikes a spacecraft surface (normal to the velocity vector) at a translational energy of approximately 5 eV.[1,8,9] It is certainly the case that gas-phase abstraction and insertion reactions of O (^{3}P) with hydrocarbons exhibit dynamic barriers of the order of 0.05-0.20 eV.[10-14]

The idea that the O atom reaction with polymers is translationally activated is supported by some recent laboratory investigations. Ferguson[9] has reported that O^+, impacting at kilovolt energies, reacts even faster with Kapton than ambient oxygen in low Earth orbit. The comparability of the reactions of oxygen atoms and ions however, may be open to some doubt. Tennyson et al.[15] reported that oxygen atoms with a translational energy of approximately 0.14 eV, produced from a microwave discharge atomic beam source, apparently react with Kapton much more slowly than do the 5 eV atoms encountered on-orbit. However, their absolute reaction probabilities are somewhat uncertain inasmuch as their experimental geometry renders measurement of the oxygen atom beam flux difficult. The flux that Tennyson et al. calculate for their source is an upper limit (as they point out) and so the reaction probabilities they report are lower limits.

The experimental and analytical support for the notion that O atom reactions with organic polymers are translationally activated has been by no means unanimous. Work from this laboratory reported earlier[9] showed that atomic oxygen striking Kapton surfaces at a translational energy of 1 eV reacted at a rate indistinguishable from orbital reaction rates. Furthermore, the analysis of the thermal mass loss data of Hansen et al.[7] is not straightforward. Depending upon the assumptions one makes about atomic oxygen production and transport in Hansen's experiments, one calculates absolute O atom reaction efficiencies in those experiments which vary by more than two orders of magnitude.[9,16]

The question of the translational energy dependence of the reaction of atomic oxygen with polymers is not a matter of mere academic interest. If the reaction rate were insensitive to translational energy (below 5 eV), there would be two major implications:

1) Spacecraft materials could be screened for stability (or lack thereof) to exposure to the residual atmosphere in low Earth orbit using equipment that is considerably less expensive and less complex than currently used or proposed atomic beam facilities.

2) One would be obliged to consider that spacecraft surfaces covered with organic polymers not directly exposed to atmospheric impingement may be eroded by the atomic oxygen that scatters (presumably at reduced velocity) from the exposed surfaces.

Experimental

Atomic Beam Apparatus

The beam apparatus used to perform these experiments has been described elsewhere.[17] It consists of a four-chamber differentially pumped vacuum system. (See Fig. 1.) The oxygen beam source is mounted in the first chamber, which provides differential pumping for the source. The second and third chambers provide for additional pressure reduction between the source and the target. Chamber 2 also contains a beam flag and chopper to aid in analysis of the beam composition and velocity.

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§Kapton is a registered trade name of E. I. Dupont de Nemours & Co., Inc.

The fourth chamber contains the solid target, mounted in a temperature-controlled holder on a three-axis plus rotation precision manipulator. The fourth chamber also houses a quadrupole mass spectrometer used to measure beam composition and velocity.

A conical nickel skimmer, 0.9 mm in diameter, forms the connection between the first and second chambers. The ⅔ and ¾ connections are round holes, approximately 2.5 mm in diameter.

During sample exposures, the pressures in chambers 1-4 were approximately 5×10^{-5}, 1×10^{-6}, 5×10^{-7}, and 2×10^{-7} Torr, respectively.

Atomic Oxygen Source

Oxygen atoms were produced by inducing a microwave-sustained discharge in a gas mixture containing 0_2. The beam source used in this experiment (see Fig. 2) employs a cavity very similar to that described in detail by Murphy and Brophy.[18] The cavity is a 3¼ wave foreshortened coaxial type with microwave power coupling and cavity tuning of the Evenson design.[19] Power was supplied to the cavity by a 2450 MHz magnetron power supply. The discharge tube was fused silica, 6 mm in diameter, with an orifice diameter of 1.0 mm.

The beam composition and velocity were measured using the quadrupole mass spectrometer. The formula of Miller and Patch[20]

$$Y=\frac{[0]}{[0_2]}=P\left[\frac{\sigma(0_2)}{\sigma(0)}\right]\left[\frac{1}{\eta}\,\frac{I(0)}{I(0_2)}-1\right] \quad (1)$$

is used to calculate the ratio of $0{:}0_2$ in the mass spectrometer ionizer. In Eq. (1), P is the probability of dissociative ionization of 0_2; $\sigma(0_2)$ and $\sigma(0)$ the cross sections for ionization of 0_2 and 0, respectively; $I(0)$ and $I(0_2)$ the mass spectrometer signals for mass 16 and 32, respectively; and η the ratio of those two signals with the source discharge off. The velocities of various species in the beam were measured by mechanically chopping short pulses (approximately 20 μs wide) and measuring the time for the beam pulse to travel from the chopper to the mass spectrometer.

In earlier tests using this source, it was found that a mixture of approximately 10% 0_2, 1% H_20 diluted in helium provided the best compromise between the competing demands for high flux and low pressure in the apparatus.[21] The addition of a small amount of water to the discharge mixture produces a nearly fivefold enhancement in the fraction of molecular oxygen dissociated. (This effect has been documented by other investigators.[22]) Figure 3 shows mass spectra of the beam, with and without the discharge on.

The measurement of an absolute reaction rate or efficiency in an experiment of this type requires a knowledge of the absolute flux of atomic oxygen in the beam. Measuring or calculating that flux is, at best, problematical. Two experimental approaches (based on calibrating the mass spectrometer absolutely) and one approximate calculation were used to ascertain the beam flux. These approaches are described below.

The experimental approaches to measuring the beam flux were those used in earlier experiments employing this facility.[23] Each was intended to calibrate the sensitivity of the mass spectrometer to molecular oxygen. The first was to add 0_2 directly into the detector chamber, measuring the added oxygen pressure with a ultrahigh-vacuum ionization gage. The second was to measure the beam signal with low pressures of pure 0_2 in the beam source. Treating the source at low pressures as essentially effusive allows one to compute an effective beam density at the ionizer.

These two approaches agreed within a factor of five for the current facility geometry, with the static gas addition implying a greater sensitivity. The direction of this discrepancy is intuitively satisfactory since one can expect the ionization volume of the mass spectrometer to be greater for a static gas, entering the ionizer from all directions, to be greater than for a directed beam.

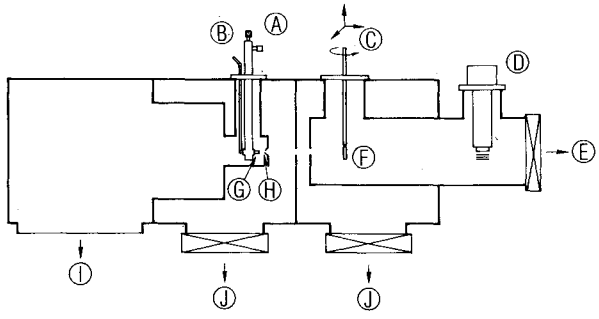

Fig. 1 Atomic beam facility schematic: A) microwave cavity, B) source gas inlet, C) three axis plus rotation precision manipulator, D) quadrupole mass spectrometer, E) 350 liter/s^{-1} turbomolecular pump, F) temperature-controlled sample mount, G) source nozzle, H) 16 in. oil diffusion pump, I) 10 in. oil diffusion pump with liquid nitrogen baffle.

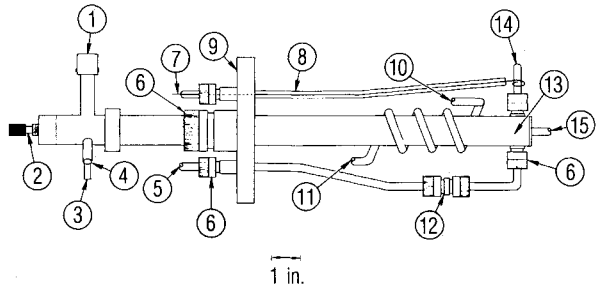

Fig. 2 Microwave discharge atomic beam source: 1) microwave power connection, 2) Gavity tuning adjustment, 3) coupling adjustment, 4) cooling gas exit, 5) source gas inlet, 6) Ultra-Torr® compression fitting, 7) ignition electrode, 8) glass insulator, 9) mounting flange (O-ring sealed), 10) cooling water inlet, 11) cooling water outlet, 12) Ultra-Torr® union, 13) quartz discharge tube, 14) nozzle, 15) cooling gas inlet.

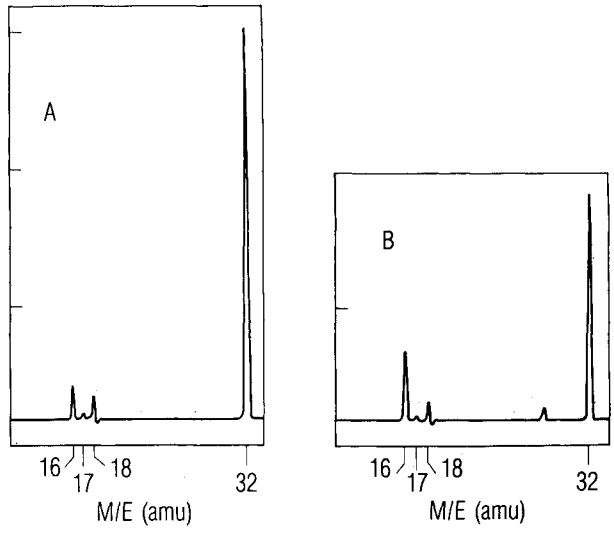

Fig. 3 Mass spectrum of atomic beam: a) discharge off; b) discharge on. (M/e values of 16,17,18, and 32 correspond to O^+, OH^+, H_2O^+, and O_2^+, respectively.)

Table 1 Microwave discharge beam source characteristics

Source feed gas	
Composition	$He/O_2/H_2O$: 90/10/1
Pressure	10 Torr
Microwave excitation	
frequency	2450 MHz
Power	70 W
Performance	
$[O]/[O_2]$	1.8–2.2
Dissociation	50%
Velocities	
O	1.30 $km \cdot s^{-1}$
O_2	1.12
He	1.45
O flux on target	$>2\times10^{15}$ $cm^{-2}\cdot s^{-1}$

Once the calibration of the mass spectrometer to 0_2 was known, the atomic oxygen density in the ionizer could be computed absolutely from the relative number density measurement described above. The beam flux at the target was then computed by multiplying the apparent number density at the mass spectrometer by the nominal beam velocity and by the appropriate factor to account for the locations of the source, target, and mass spectrometer. The typical lower limit to the 0 atom flux measure this way was 2×10^{15} $cm^{-2}\cdot s^{-1}$, at the target.

The approximate computational scheme of Lam[24] was used to estimate the atomic oxygen flux as well. In this scheme, the properties of the mixed gas jet are modeled by assuming the gas to be a single component with thermal and collisional properties equal to the weighted average of those of the constituent gases. Assuming perfect alignment of the system and no interaction between the beam and the skimmer, this computation indicates that the atomic oxygen flux should be approximately 1.6×10^{16} $cm^{-2}\cdot s^{-1}$. Because this calculation ignores the shielding effect of the skimmer, it overestimates the flux by a factor of approximately two.[25]

It is assumed that these computed and measured values of flux bracket the true value.

Table 1 summarizes the operating conditions of the source for these experiments.

Sample Preparation

The samples that were bombarded were disks of 5 mil (130 μm) thick Kapton 0.9 in. (23 mm) in diameter. Each film disk was cleaned with sequential rinses of trichloroethene, acetone, methanol, and deionized water. The solvents were Baker analyzed reagent grade. Following the rinses, the samples were blown dry with nitrogen. The polymer disks were bonded to 1 in. diam fused-silica flats using Dow Corning 93-500 space grade encapsulant as the adhesive. The siloxane material was mixed according to the manufacturer's instructions and vacuum degassed before use. The adhesive was allowed to cure for at least 7 days at room temperature before the samples were bombarded.

Results and Discussion

Three samples were bombarded, two for a total of approximately 6 h and one for 3 h. Thus, the samples received an atomic oxygen fluence¶ in excess of 2×10^{19} or 4×10^{19} cm^{-2}. After the bombardments, the samples were removed from the vacuum system and examined by the naked eye and by electron or optical microscopy.

In no case was there any sign of reaction. If the reaction had been proceeding at the rate observed for 1 eV oxygen atoms,[8] then at least 0.3 μm of Kapton would have been removed and the characteristic surface roughening caused by the etching reaction would have been readily visible.

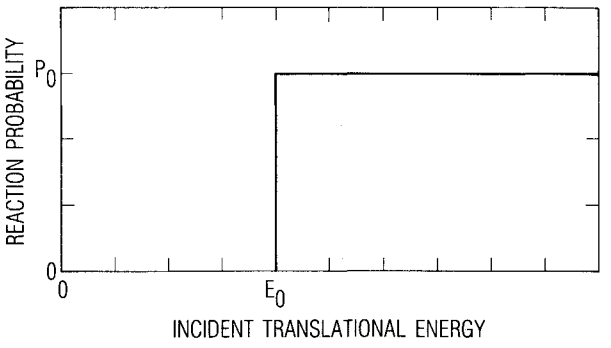

Fig. 4 A simple model for threshold behavior in O atom reactions in solids.

Interpretation of a negative result such as this one is always difficult. One must consider whether the reaction was inhibited through some unrecognized error in the experimental procedure. One possibility is that there was some source of contamination in the sample exposure chamber that was deposited on the Kapton surface and effectively prevented reaction. It has been shown through flight and laboratory experiments that thin siloxane or metal films can inhibit the oxidation of polymers.[2,6]

To test for this problem, a thin silver film was exposed to the oxygen beam for 2 h, following the same procedure used in the Kapton bombardments. Both low-velocity atomic beam experiments[26] and Shuttle-borne experiments[4] have shown silver to be rapidly oxidized by $0(^3P)$. A characteristic black spot in the area where the beam struck the silver film was observed, confirming that oxygen atoms were striking the surface and reacting.

The fact that no significant reaction of atomic oxygen with Kapton was observed in the experiments reported here, together with the results of Tennyson *et al.*,[15,27] drive one to the conclusion that the hypothesized strong positive dependence on incident translational energy of the reaction of $0(^3P)$ with polyimide films is real. In this characteristic, the gas/solid reactions of $0(^3P)$ with organics appear similar to the analogous gas-phase reactions.

It is useful to inquire whether the data now available allow one to infer a value for a dynamic threshold (in incident translational energy) for the reaction of atomic oxygen with Kapton. An examination of a simple model for the dynamics of 0 atom etching reactions can provide a basis for such an inquiry.

Figure 4 portrays a dynamic behavior for the probability P that an 0 atom striking a polymer surface will react, which can be summarized as

$$\begin{aligned} P &= P_0 \qquad E_t \geq E_0 \\ P &= 0 \qquad E_t < E_0 \end{aligned} \tag{2}$$

where E_t is the incident translational energy of the 0 atom and E_0 the threshold energy.

If one were to perform a series of reaction probability measurements with a perfectly monoenergetic beam and variable energy, the measurements would map precisely this behavior (assuming the model to be the correct one.) However, if one were to expose a reactive polymer to a gas containing atomic oxygen in thermal equilibrium, then one would measure an effective reaction probability,

$$P_{\text{eff}} = P_0 \times F(E_0{:}T) \tag{3}$$

where T is the temperature of the gas and $F(E_0{:}^T)$ the fraction

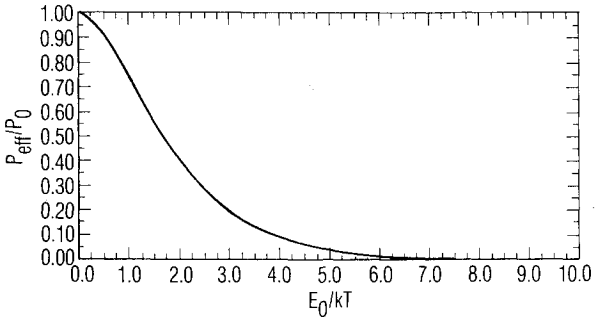

Fig. 5 Plot of P_{eff}/P_0, the function $\Gamma(2,E_0/kT)$ vs E_0/kT.

of 0 atoms that strike the polymer surface with translational energy greater than E_0.

Under the assumption that the gas always remains in thermal equilibrium, $F(E_O{:}T)$ can be calculated from the simple kinetic theory given by

$$F(E_0{:}T) = (2,E_0/kT) \tag{4}$$

where k is Boltzmann's constant and $\Gamma(x,y)$ the incomplete gamma function of the second kind.[28] Figure 5 shows a plot of $\Gamma(2,y)$ for $0<y<10$.

The experiments of Hansen et al.[7] can be analyzed under the assumption of thermal equilibrium.[16] Such an analysis yields the result that the rate of reaction of 0 atoms at 340 K is approximately 1.2% of the rate for orbital velocity (5 eV) 0 atoms. If one takes the orbital rate to be P_0, then Eq. (4) implies a threshold energy of approximately 0.2 eV. This value is consistent with those observed for gas-phase reactions of 0 (^{3}P) with organic molecules.[10-14]

The experimental work reported in this paper used an atomic oxygen beam with a most probable energy of 0.14 eV. However, the distribution of velocities from this source is very narrow. A calculation of the cumulative distribution of 0 atom velocities to be expected from this source suggests that only approximately 5% of the 0 atoms emanating from the source have translational energies in excess of 0.2 eV. Therefore, the fact that no evidence of reaction was observed in this work is not inconsistent with a dynamic threshold of 0.2 eV. Any more precise definition of that threshold, if indeed the simple behavior postulated is correct, will require additional experimentation.

It is not possible to assign an upper limit to the reaction probability based on an observation of no reaction. However, further work by Tennyson and his co-workers using a beam source, similar to the one used here, employing substantially longer exposures than this work,[29] has shown reaction probabilities of 0.01-0.05 times orbital probabilities.[3,27] Under the model proposed in this paper, one would interpret their reaction probabilities as being due to reaction by the high-energy tail of their source.

It is difficult to draw general conclusions about the dynamics of 0 atom reactions with polymers from the limited data available. However, it is not unreasonable to suppose that the oxidation of organic polymers other than Kapton, including paint binders, will exhibit a similar dependence on 0 atom translational energy, although the value of the dynamic threshold to reaction is likely to vary from material to material. This suggests that there is some finite number of surface reflections beyond which LEO atomic oxygen will not be significantly reactive to polymers and paints.

Acknowledgment

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