

# Reaction of Atomic Oxygen with Polyimide Films

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The rate of removal of Kapton† by chemical reaction with atomic oxygen impacting at a translational energy of approximately 1 eV has been measured under conditions that approximate atmospheric bombardment of spacecraft surfaces in low Earth orbit. The average reaction efficiency was found to be approximately  $(2 \pm 1) \times 10^{-24}$  cm<sup>3</sup>/O atom, independent of surface temperature over the range of 300-400 K. This value is in good agreement with the reaction rates inferred from low Earth orbit exposures on various Space Shuttle flights.

## Nomenclature

|            |  |
|------------|--|
| $B$        | = product of an oxygen atom reaction with a solid  |
| $E_t$      | = atomic oxygen translational energy   |
| $F_O$      | = flux of atomic oxygen  |
| $F_B$      | = flux of reaction products  |
| $k_1, k_2$ | = rate coefficient for desorption and reaction, respectively, of adsorbed atomic oxygen                                |
| $k_3$      | = rate coefficient for desorption of adsorbed products   |
| $k'$       | = $k_2 k_3 / (k_2 + k_3)$  |
| $k''$      | = $k_1 k_3 / (k_2 + k_3)$  |
| $p$        | = average reaction probability or efficiency; the flux or number of products divided by the flux or fluence of reagent |
| $P_1$      | = sticking probability for a gas-solid collision   |
| $S$        | = instantaneous density of active surface sites  |
| $S_0$      | = total density of active surface sites  |

## Subscripts

|     |                              |
|-----|------------------------------|
| $g$ | = gas-phase atom or molecule |
| $s$ | = adsorbed atom or molecule  |

## Introduction

IN low Earth orbit (LEO), altitudes of 200-700 km, a spacecraft experiences bombardment by the ambient atmosphere, the predominant species of which is neutral atomic oxygen.<sup>1</sup> Although the ambient gas temperature is only on the order of 1000 K, the 8 km-s<sup>-1</sup> velocity of the spacecraft causes the oxygen atoms to strike satellite surfaces at a relative kinetic energy of 5 eV (500 kJ-mole<sup>-1</sup>). At Shuttle altitudes the atomic oxygen density is on the order of  $10^9$  cm<sup>-3</sup>, which corresponds to a flux of about  $10^{15}$  cm<sup>-2</sup>-s<sup>-1</sup>. These conditions present a regime of gas-surface chemistry, which has been the subject of very little experimental investigation because of the difficulties inherent in reproducing them in the laboratory.

Various materials exposed to the LEO environment on the Shuttle Orbiter have been reported to undergo erosion which has been ascribed to the action of atomic oxygen. These include organic polymers,<sup>2,5</sup> organic paints,<sup>5,6</sup> carbon, and osmium.<sup>7</sup> Perhaps the material whose erosion in LEO has been most extensively studied is the DuPont polyimide Kapton, which is widely used on spacecraft thermal control blankets.

The fact that organic polymers were eroded in low Earth orbit was not surprising; the reaction of atomic oxygen with polymers has been known for some time.<sup>8</sup> However, the apparent rate at which Kapton reacted on orbit was over two orders of magnitude greater than one would have predicted on the basis of published laboratory studies of the effect of atomic oxygen on polymers.<sup>8</sup>

This paper reports the results of a study of the reaction of Kapton with suprathermal (1 eV) atomic oxygen. These experiments were performed using an atomic beam facility assembled specifically for the study of atmospheric effects in low Earth orbit.<sup>9</sup>

## Experimental

The apparatus used to perform these laboratory measurements consists of a three-chamber differentially pumped vacuum system (see Fig. 1). The oxygen atom beam source is attached to the first chamber, which provides differential pumping for the source. The second chamber contains the sample to be bombarded, which is temperature controlled and surrounded by a liquid-nitrogen-cooled shroud to inhibit contamination. The third chamber contains a quadrupole mass spectrometer used to measure beam composition and intensity. During the sample exposures, the pressures in chambers 1, 2, and 3 were approximately  $5 \times 10^{-4}$ ,  $5 \times 10^{-6}$ , and  $3 \times 10^{-7}$  Torr, respectively. The primary residual gas in the first and second chambers was helium.

The oxygen atom source has been described elsewhere,<sup>9</sup> and is similar to another source described in the literature.<sup>10</sup> A dc arc dissipating approximately 16 kW heats a flowing stream of helium at atmospheric pressure. A small quantity of O<sub>2</sub> (approximately 2% of the total gas flow) is injected into the flow downstream of the arc, where it is thermally dissociated into oxygen atoms by the hot helium. A small portion of the hot gas mixture expands into the vacuum system producing a suprathermal beam comprised of a mixture of helium, atomic oxygen, and molecular oxygen. The ratio of atomic to molecular oxygen in the beam varies over the range of 0.6-0.9. The velocity of the beam is approximately 3.5 km-s<sup>-1</sup>.

The samples bombarded were disks of 5-mil-thick Kapton, 0.9 in. in diameter. Each film disk was cleaned with sequential rinses with 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 quartz flats using Dow Corning 93-500 space-grade encapsulant as the adhesive. The siloxane material was mixed according to manufacturer's instructions and vacuum degassed before use. The adhesive was allowed to cure for seven days at room temperature before the samples were bombarded.

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†"Kapton" is a registered trade name of E. I. DuPont de Nemours and Co.

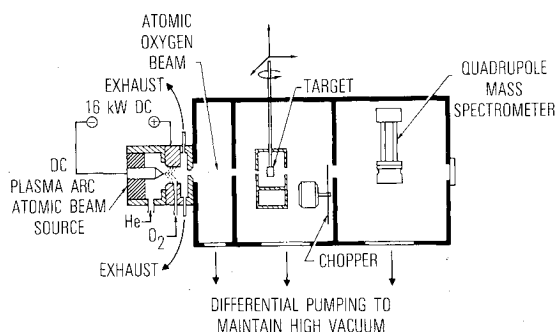


Fig. 1 High-energy oxygen atom surface chemistry apparatus.

Table 1 Experimental conditions

| Sample temperature, K | Beam composition     | Average O-atom flux, $10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ | O-atom fluence, $10^{19} \text{ cm}^{-2}$ |
|-----------------------|----------------------|---|---|
| 300                   | He/O <sub>2</sub> /O | $5.5 \pm 2.8$   | $6.3 \pm 3.2$                             |
| 300                   | He/O <sub>2</sub> /O | $4.2 \pm 2.1$   | $5.6 \pm 2.8$                             |
| 338                   | He/O <sub>2</sub> /O | $6.3 \pm 3.1$   | $6.5 \pm 3.8$                             |
| 393                   | He/O <sub>2</sub> /O | $6.1 \pm 3.1$   | $6.7 \pm 3.5$                             |
| 300                   | He                   | —   | —   |

Table 1 summarizes the beam conditions for each of the five Kapton sample exposures. The beam flux was measured periodically throughout the sample exposures. The time-weighted averages of the flux, accounting for variations in the apparent fractional dissociation and the absolute beam intensity, are reported in Table 1. The absolute value of the flux of atomic oxygen is subject to a systematic uncertainty estimated to be  $\pm 50\%$  due to uncertainty in the mass spectrometer calibration.<sup>11</sup> The total exposure times were about 3 h, thus producing a fluence<sup>†</sup> of atomic oxygen on the target of about  $6 \times 10^{19} \text{ cm}^{-2}$ . Note that one sample was exposed to the dc arc-heated beam operating with pure helium (for approximately the same period of time employed in the oxidative bombardments). This bombardment was performed to discern the effects of oxygen from any effects of helium species or ultraviolet light in the beam.

The atomic beam was collimated to subtend a roughly circular 7-mm-diam spot on the target. The extent of erosion was ascertained *ex situ* by measuring the surface profile of the sample at the exposure edge with a stylus profilometer (Sloan Dektak FLM).

## Results

The exposed area of the samples subjected to the oxygen-containing beam was visibly roughened in a manner similar to flight samples. The Kapton disk exposed to the pure helium beam showed no such effect. Figure 2 shows electron micrographs of areas of the Kapton exposed to and shielded from the oxygen-containing beam. The uniformly roughened appearance of the exposed area is reminiscent of the appearance of Kapton surfaces exposed to the low Earth orbit environment.<sup>3</sup> Microscopic examination of the Kapton disk exposed to the pure helium beam revealed no alterations to the surface within the bombarded area. This "control" experiment shows that uv light or some helium species contained in the beam is not solely responsible for the reaction observed when the He/O<sub>2</sub>/O beam is directed onto the Kap-

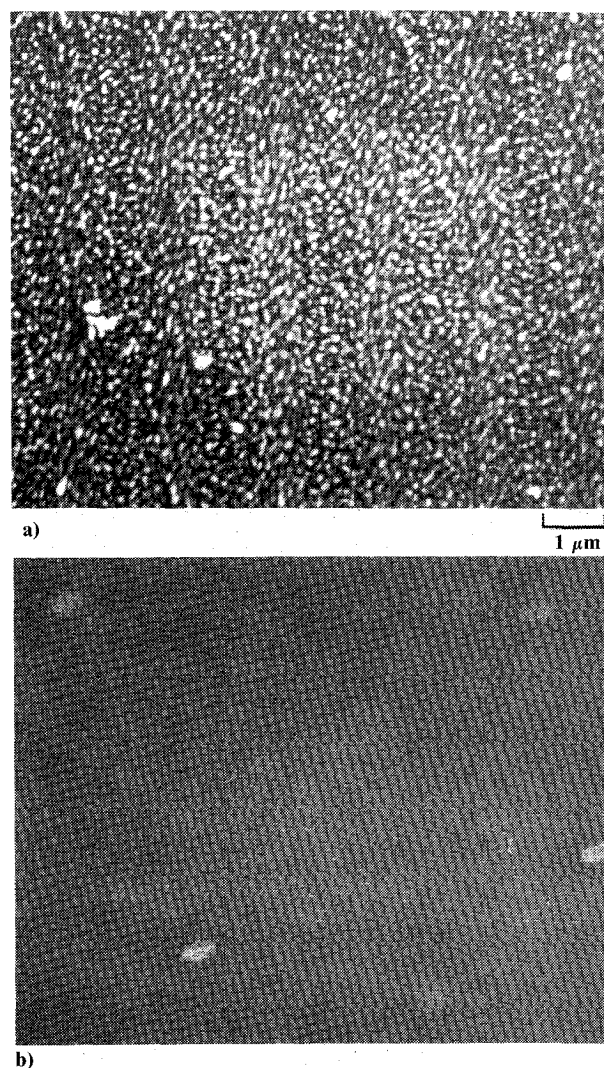


Fig. 2 Electron micrographs of Kapton surfaces: a) exposed to He/O<sub>2</sub>/O beam, b) shielded from beam. Microscope conditions were 10-kV electron energy, and  $10,000\times$  magnification.

ton. (However, it does not rule out the possibility of some synergy between oxygen in the beam and these other components. An experiment to resolve this uncertainty is physically possible, but beyond the scope of our investigation at this time.)

Several measurements (in duplicate) of the depth of erosion at various locations around the edge of the exposed area of the samples bombarded by the He/O<sub>2</sub>/O beam were performed. Figure 3 shows three such profilometer traces. Table 2 summarizes the results of these measurements.

It has become customary to report average probabilities for atomic oxygen reaction with polymers as the thickness of material removed divided by the incident fluence of atomic oxygen.<sup>2,3</sup> Table 2 lists the reaction efficiencies obtained if one ascribes the removal of material of the laboratory samples to the action of the atomic oxygen in the beam. Also shown in Table 2 are average mass-loss rates calculated using a nominal density<sup>12</sup> of  $1.4 \text{ g cm}^{-3}$ .

In calculating these reaction probabilities it has been assumed that only *atomic* oxygen in the beam is reactive. The justification for not ascribing any fraction of the erosion to the action of helium and uv light in the beam is presented above. Ignoring direct reaction with molecular oxygen in the beam is justified by the well-known stability of Kapton to degradation by molecular oxygen,<sup>12</sup> even at high temperature. Collisional dissociation of molecular oxygen in the

<sup>†</sup>Fluence is the time integral of flux, and therefore has units of atoms incident per unit area. This quantity is also sometimes called the integrated flux.

**Table 2** Average probabilities for the reaction of atomic oxygen with Kapton

| Sample temperature, K | O-atom fluence, $10^{19} \text{ cm}^{-2}$ | Thickness loss, $\mu\text{m}$ | Reaction probability, $10^{-24} \text{ cm}^3/\text{O atom}$ | Reaction probability, amu/O atom <sup>a</sup> |
|-----------------------|---|-------------------------------|---|---|
| 300                   | $6.3 \pm 3.2$                             | $1.32 \pm 0.13$               | $2.1 \pm 1.1$   | $1.8 \pm 0.9$                                 |
| 300                   | $5.6 \pm 2.8$                             | $0.98 \pm 0.08$               | $1.7 \pm 0.9$   | $1.5 \pm 0.7$                                 |
| 338                   | $6.5 \pm 3.8$                             | $0.92 \pm 0.19$               | $1.4 \pm 0.9$   | $1.2 \pm 0.7$                                 |
| 393                   | $6.7 \pm 3.5$                             | $1.03 \pm 0.17$               | $1.5 \pm 0.9$   | $1.3 \pm 0.7$                                 |

<sup>a</sup> 1 amu =  $1.66 \times 10^{-24}$  g.**Table 3** Comparison of laboratory and flight measurements of average probabilities for reaction of atomic oxygen with Kapton

| Kapton temperature, K | Reaction probability, $10^{-24} \text{ cm}^3/\text{O atom}$ |                    |                    |
|-----------------------|---|--------------------|--------------------|
|                       | This work   | STS-5 <sup>a</sup> | STS-8 <sup>b</sup> |
| 300                   | $2.1 \pm 1.1$<br>$1.7 \pm 0.9$                              | $2.3 \pm 0.9$      | —                  |
| 338                   | $1.4 \pm 0.9$   | $2.0 \pm 0.8$      | $3.0 \pm 1.2$      |
| 393                   | $1.5 \pm 0.9$   | $2.1 \pm 0.9$      | $2.9 \pm 1.2$      |

<sup>a</sup> See Table 3 of Ref. 2. Nominal error is  $\pm 40\%$ . <sup>b</sup> See Table 5 of Ref. 3. Nominal error is  $\pm 40\%$ .

beam followed by reaction on the surface is unlikely since the impact energy of molecular oxygen (approximately 2 eV) in these experiments was not sufficient, in itself, to promote collisional dissociation of the  $\text{O}_2$ .

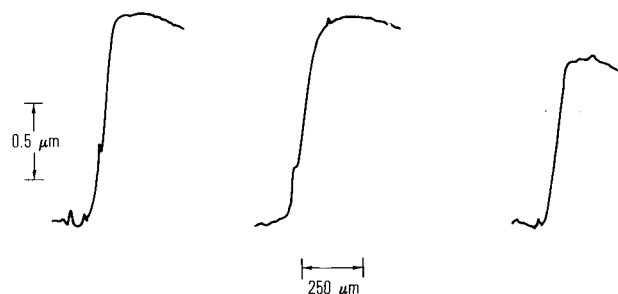
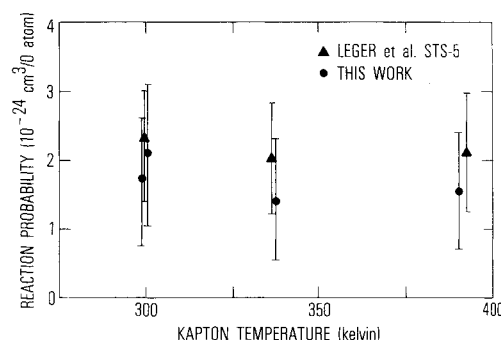
The uncertainties quoted for the reaction probabilities include the uncertainty in the value of the atomic oxygen flux and the range of values measured for the depth of erosion on each sample. One may readily see that it is systematic uncertainty in the atomic oxygen flux, used to compute the fluence, that dominates the uncertainty in the inferred average reaction probability.

### Discussion

Two experiments entitled "Evaluation of Oxygen Interaction with Materials" were flown on the fifth and eighth flights of the Shuttle Orbiter (STS-5 and STS-8). Each of these experiments contained temperature-controlled arrays of polymer film strips, including a number of samples of Kapton.<sup>2,3</sup> The total fluences of atomic oxygen incident upon the samples were approximately  $1 \times 10^{20}$  and  $3.5 \times 10^{20} \text{ cm}^{-2}$  for the STS-5 and STS-8 flights, respectively. The results of this experiment are compared to the flight results in Table 3.

Figure 4 shows a comparison between the average reaction probabilities observed on STS-5<sup>2</sup> and in the laboratory experiments reported here. The laboratory results are plotted with those of STS-5 because the fluence encountered on that flight was more nearly equal to that used in the laboratory. Since the surface of the polymer is significantly roughened by the reaction process, it is reasonable to suppose that its effective surface area, and, therefore, the total reaction rate, are increasing. Although the STS-8 and STS-5 results do agree within their ranges of uncertainty, the differences in the mean values may suggest such an effect. Furthermore, investigators at NASA Johnson Space Center have observed that reaction rates of Kapton with atomic oxygen in a room-temperature flow tube increase with time.<sup>13</sup> If one assumes that all other conditions were constant during these flow-tube experiments, this observation suggests that the instantaneous reaction probability is increasing as the reaction proceeds (that is, as the oxygen fluence accrues). Thus, one must not discount the possibility that the sort of average reaction probability that one customarily quotes for the reaction of atomic oxygen with spacecraft materials depends on the fluence of oxygen to which the material was subjected.

The agreement between the laboratory results reported here and the STS-5 data, and indeed even the STS-8 results,

**Fig. 3** Kapton sample profilometer traces. The stylus was scanned from the eroded area (left) to the shielded area (right).**Fig. 4** Comparison of STS-5 and laboratory measurements of the average reaction efficiency of the O + Kapton reaction as a function of Kapton temperature. Laboratory and flight results are for identical nominal temperatures; laboratory results are offset along the temperature axis for clarity.

is quite good in comparison to the uncertainties in the data. Neither the flight nor the laboratory data show a discernible dependence on the temperature of the Kapton. This conclusion may be drawn firmly inasmuch as the uncertainties in the reaction probabilities inferred from both the laboratory and flight experiments are dominated by a systematic uncertainty in the methods used for computing the atomic oxygen fluence. Thus, while the degree to which the three sets of data agree or disagree is clouded by this uncertainty, the relative values of reaction probability are well determined within each of the laboratory, STS-8, and STS-5 data sets. The constancy of this reaction probability over this temperature range is in marked contrast to the rather substantial activation energy with respect to surface temperature of the reaction probability of atomic oxygen with carbon.<sup>11</sup>

However, these average reaction probabilities are much greater than those that might be inferred from the room-temperature flow-tube work of Hansen et al.<sup>8</sup> Hansen and co-workers report a mass-loss rate for "polyimide" of  $4.2 \times 10^{-7} \text{ g-cm}^{-2}\text{-s}^{-1}$  in a low-pressure gas containing  $10^{14}$ - $10^{15} \text{ cm}^{-3}$  of O atoms. They report a sample temperature of less than or equal to 343 K. Using the temperature to obtain an average thermal velocity of  $6.7 \times 10^4 \text{ cm-s}^{-1}$ , one computes a flux of  $0.17$ - $1.7 \times 10^{19} \text{ cm}^{-2}\text{-s}^{-1}$  and an average

reaction probability of  $0.15\text{--}1.5 \times 10^{-1}$  amu/O atom or  $0.17\text{--}1.7 \times 10^{-25}$  cm<sup>3</sup>/O atom at a nominal polymer density of  $1.4 \text{ g}\cdot\text{cm}^{-3}$ .

The atomic oxygen flux for Hansen's experiment calculated by the simple equilibrium assumption used above is, of course, an upper limit. Processes such as gas-phase reactions of the atomic oxygen or consumption of atomic oxygen at the reacting polymer surface may be sufficiently faster than diffusion of the O atoms to prevent the maintenance of thermal equilibrium.<sup>14</sup> Thus the reaction probability calculated for Hansen's experiment must be considered an average lower bound.

Even admitting the uncertainty in this simple analysis of Hansen's reported mass-loss rates, this discrepancy is so large that it may not be dismissed without some consideration of its having an origin in either the kinetics or dynamics of the reaction of atomic oxygen with the polymer rather than in the kinetics of oxygen atom transport in the tube. Thus, one must look to the differences in the nature of the exposure of the polymer to atomic oxygen in the three sorts of experiments.

It is unlikely that the fact that in the flow tube the oxygen atoms strike the surface at random angles can account for this discrepancy. Because an ordinary (as opposed to single-crystal) surface is rough on a molecular scale, even in the case of the laboratory experiments using a collimated beam, the angle at which the oxygen atom actually strikes the surface is random. One might suppose, however, that the surface of the polymer is so roughened by the reaction that it presents an array of pits that act as effective traps, providing for multiple encounters of oxygen atoms within some range of angles near the average surface normal. However the fact that STS-5 samples, which were exposed primarily to a "sweeping" velocity vector,<sup>2</sup> which provided all angles of impact, and the STS-8 samples, which received the preponderance of their oxygen fluence normal to the velocity vector,<sup>3</sup> showed similar, if not equal, mass-loss rates, shows that such an effect cannot account for the discrepancy.

The most obvious difference among the exposure conditions of Shuttle flight, the atomic beam experiments of this work, and the flow tube of Hansen et al. is the translational energy with which the oxygen atom strikes the polyimide surface. This energy is approximately 5, 1, and 0.04 eV (500, 100, and 4 kJ·mole<sup>-1</sup>) for the Shuttle, beam, and flow tube, respectively. One might naturally suppose that increasing the impact energy might accelerate the reaction rate. Figure 5 shows a plot of reaction probability as a function of the reciprocal of the translational energy of the O atom. The solid line is a fit to these data of the form

$$p = 1.8 \exp[-0.18/E_t] \quad (1)$$

for  $p$  in amu/O atom and  $E_t$  in eV. (One should note that there is no reason, a priori, to assume an Arrhenius-type behavior for  $p$ .) Although this plot very nearly comprises a straight line through two points, the inferred "activation energy" of 0.18 eV (17 kJ·mole<sup>-1</sup>) is not unreasonable if one interprets it as the barrier to the initial chemisorption of the oxygen atom on the polyimide surface.<sup>15</sup>

Another significant difference among the three exposure conditions is in the flux of atomic oxygen striking the polyimide surface. This flux is approximately  $3 \times 10^{14}$  and  $5 \times 10^{15}$  for the Shuttle and beam experiments, respectively, and has been taken to be  $0.7\text{--}7 \times 10^{19}$  cm<sup>-2</sup>·s<sup>-1</sup> in the analysis of the flow-tube experiment presented above.

The simplest kinetic model one can assume for the process of O-atom erosion of a polymer is the first-order mechanism shown below.

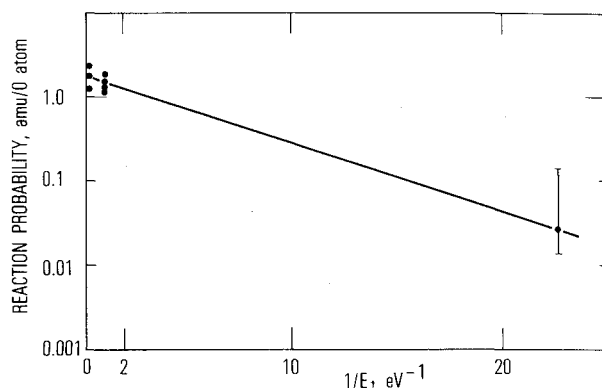


Fig. 5 Plot of  $\log_{10}(p)$  vs  $1/E_t$ .

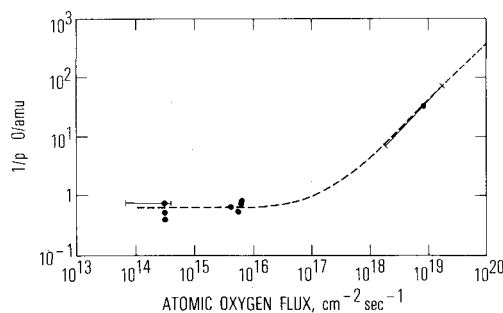


Fig. 6 Plot of  $\log_{10}(1/p)$  vs  $\log_{10}(F_O)$ .



An oxygen atom O strikes a surface and is absorbed, with some clean surface sticking probability,  $P_1$ . The O atom may spontaneously desorb without reacting with a rate characterized by the coefficient  $k_1$ , or may react to form the absorbed product B, with a rate characterized by the coefficient  $k_2$ . The product may then desorb at rate  $k_3$ .

The steady-state flux of products  $F_B$  can be calculated if one assumes that the incoming flux of reagent is constant at  $F_O$  and the total number of potentially reactive surface sites (the sum of  $[S]$ ,  $[B_s]$ , and  $[O_s]$ ) is constant at  $S_0$ . The steady-state product flux is given by

$$F_B = k' P_1 F_O / [k' + k'' + P_1 F_O / S_0] \quad (5)$$

The reaction probability  $p$  is then merely  $F_B / F_O$ . Thus a plot of the reciprocal of the reaction efficiency against the flux of atomic oxygen should yield a straight line:

$$1/p = 1/P_1 + k_1/k_2 P_1 + F_O/k' S_0 \quad (6)$$

The fact that the overall reaction rate is relatively insensitive to the Kapton surface temperature suggests that the products of the reaction are weakly bound to the substrate and, therefore, the desorption rate coefficient is large. In the limit that  $k_3 > k_2$ , the slope of Eq. (6) reduces to  $1/k_2 S_0$ .

Figure 6 shows a plot of the reciprocal of the reaction probability vs the flux of atomic oxygen. The smooth curve is a fit of the form

$$1/p = 0.65 + 4.0 \times 10^{-18} F_O \quad (7)$$

for  $p$  in amu/O atom and  $F_O$  in  $\text{cm}^{-2}\text{s}^{-1}$ . Again this is a plot over a wide range of flux and reaction probability based on very few data and, therefore, it is necessary to enquire whether these fitted parameters are physically reasonable.

Before one can make any reasonability arguments about this fit, it is necessary to convert the experimentally measured mass- or volume-loss rates to a dimensionless rate in terms of particle flux of products divided by incident flux of atomic oxygen. Since the products of the reaction of atomic oxygen with Kapton are unknown, this conversion cannot, of course, be done with any degree of certainty. However, a reasonable estimate may be made based on the presumption that the repeating unit of Kapton<sup>16</sup> is of the form  $\text{C}_{22}\text{H}_{10}\text{N}_2\text{O}_5$ . The weight of the average atom in this repeating unit is 9.8 amu. If one further assumes that each reactive oxygen atom carries away one atom from the substrate, then dimensionless reaction probabilities are approximately one-tenth of the mass-loss rate in amu/O atom.

Using this simplifying assumption, one obtains a value of approximately 0.2 for the dimensionless quantity  $k_2P_1/(k_1+k_2)$  from the intercept in Eq. (7). Thus, one concludes that  $P_1$  is approximately 0.2 if  $k_2 \gg k_1$  or 0.4 if  $k_1$  and  $k_2$  are approximately equal. (The case that  $k_1 \gg k_2$  need not be considered since this would imply that no reaction takes place.) This inferred range of values for the initial sticking probability is quite reasonable in comparison to measurements of 0.4-0.6 for the reflection probability of O atoms striking practical surfaces at thermal energies.<sup>17</sup>

When one performs the same unit conversion on the slope of Eq. (7), one obtains the result that  $k_2S_0$  is on the order of  $3 \times 10^{16} \text{ cm}^{-2}\text{s}^{-1}$ . This value implies that the density of active surface sites and the surface reaction rate are not particularly large. A low density of active sites is not unreasonable for a material such as Kapton. The average molecular weight of a polyimide is in the range of 40,000-100,000 amu.<sup>16</sup> If only the ends of the macromolecules are reactive or if a particular conformation is required for the molecule to be reactive, then a surface site density as low as  $10^{12} \text{ cm}^{-2}$  would not be surprising.

This leaves one to surmise that  $k_2$  is less than  $10^5 \text{ s}^{-1}$ . This rate coefficient might also be understood as approximating the reciprocal of the mean time for diffusion among the reactive surface sites. From the product  $k_2S_0$  and the lower limit of  $10^{12} \text{ cm}^{-2}$  on  $S_0$ , one infers an upper limit of  $10^{-8} \text{ cm}^2\text{s}^{-1}$  for the surface diffusion constant, which, indeed, is not an unreasonable value.<sup>18,19</sup>

Of course, the type of analysis of the magnitudes of the parameters of Eq. (7) that has been presented above cannot provide the basis for a firm determination of the role of the atomic oxygen flux in the discrepancy between the reaction rates inferred from the flow-tube experiments and the beam and flight experiments. The data are too sparse and too uncertain and the parameters of Eq. (7) contain too many variables. However, the values of the slope and intercept of Eq. (7) are not so unreasonable as to allow one to dismiss the notion that differences in the atomic oxygen fluxes in the two types of exposures can account for the different overall reaction efficiencies.

### Conclusions

The experimental results reported herein demonstrate that the rate of removal of Kapton in low Earth orbit can be reproduced in the laboratory by a controlled exposure of the polymer to suprathreshold neutral atomic oxygen under single collision conditions. As such, these experiments represent the first independent laboratory confirmation that Kapton erosion rates observed on the various Shuttle flights can indeed be ascribed to the action of atomic oxygen.

The relatively good agreement between the laboratory results presented here and the STS-5 results suggests that there is not a great dependence on translational energy of the

average "probability" of the reaction of atomic oxygen with Kapton over a range of impact energy from 1 to 5 eV.

Clearly the data available do not permit one to discern which, if either, of the two rationalizations of the discrepancy between the rate inferred from the thermal flow-tube work of Hansen et al.<sup>8</sup> and the suprathreshold beam and flight results is correct. Indeed it is possible that the discrepancy may result from an inability to calculate the average reaction probability correctly for the flow-tube experiment due to an imprecise knowledge of the conditions of that experiment.

A measurement of the rate of the Kapton-oxygen reaction at a translational energy of approximately 0.1 eV would be of particular use for resolving the question of whether translational energy accelerates the reaction rate. Such an impact energy is readily accessible using much more conventional atomic beam sources than the one employed in this experiment.<sup>20</sup>

### Note Added in Proof

Further calculations of the type described by Judeikis,<sup>14</sup> taking into account oxygen atom diffusion and consumption at the polymer surface, under conditions which approximate those of Hansen et al., lend credence to the notion that it is inadequacy of the simple equilibrium analysis of those data, rather than the kinetics or dynamics of O atom reactions with polymers, which accounts for the discrepancy discussed above.<sup>21</sup>

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