THE PRODUCTION OF GLOW PRECURSORS BY OXIDATIVE EROSION OF SPACECRAFT SURFACES

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Abstract. Erosion rates of organic materials were measured during a recent flight of the shuttle (STS-8). Several forms of carbon and a variety of thermosetting and thermoplastic polymers were exposed to the ram beam of atomic oxygen. Arrhenius energies of about 1000-2000 cal mole^{-1} were measured from the rate dependencies on temperature. If some simple assumptions are made about the chemical nature of the desorbed species, the data can be used to estimate production rates at surfaces in orbit under different conditions of temperature, oxygen atom flux and material surface conditions.

Introduction

Erosion of carbon and organic polymer surfaces by "active" or atomic oxygen has been known for decades [e.g., Blackwood and McTaggart, 1959; Hansen et al., 1965]. Gregory and Peters [1975] pointed out that the atmosphere in orbit at a few hundred km altitude would be at least as reactive and proposed the use of the returnable Long Duration Exposure Facility (LDEF) for a study of the effects. Although, at the time of writing, this spacecraft is still in orbit, a version of the atomic oxygen instrument was flown in 1983 on the STS-8 mission. The objectives of the experiment were to begin an investigation of the mechanisms of interaction of 5 eV oxygen atoms with solid surfaces by measuring the rate of reaction as a function of temperature and oxygen flux, and by examining the scattered distribution of atoms re-emitted from certain surfaces. In addition, a number of optical quality metal films were prepared and exposed to investigate the growth of their oxide films or any morphological changes induced by the oxygen atom beam. In this paper only the results on carbon and solid polymers is discussed.

In the context of glow, emission of reaction products from the surface may be relevant in two ways. Oxidation products may be desorbed in excited states which subsequently decay emitting radiation, or products may suffer reactive collision with another 5 eV oxygen atom producing new products in excited states. Evidence favoring the latter mechanism includes:

(a) New calculations [Rantanen, 1985; Brock, 1985] of mean-free-path of emitted species indicate large probability of collision with the ambient stream.

(b) Energetic collisions of organic molecules with oxygen atoms are expected to have a significant probability for reaction producing excited products.

(c) Emission lines from C_2 species were observed [Torr and Torr, 1985] on Spacelab 1.

(d) An extended (tens of meters) glow around the orbiter in the unresolved infrared was observed [Witteborn, 1984] from the ground during a recent shuttle flight.

Experimental Approach

The experimental approach used was necessarily very simple as no electromechanical devices such as lids, shutters, etc. were available, and no intermediate measurements could be made; i.e., only a single integral effect could be measured for each sample. Samples were nominally 1-inch discs, with the hot-plate discs only being ¼-inch diameter. For the case of the erodible materials discussed here, a bar-pattern of small rectangles of niobium was deposited on the surface using a photo-resist technique (Figure 1). The niobium was sputtered on as a uniform film ∿2000 Å thick. Although it oxidized heavily, it still served to protect the underlying carbonaceous material. The scanning electron microscope picture in Figure 2 shows both the eroded portion of a vitreous carbon disc and the part covered and protected by the niobium film. The height of the step on this sample was about 50,000 Å (5 μm). The bar-pattern allowed multiple measurements of the step-height to be made using a Dektak stylus profilometer. Amplitudes were checked using the SEM micrographs. Half of each sample was covered at all times before and during the flight, and served as a control.

Erodible surfaces studied included single crystal graphite (basal and prismatic planes), vitreous (or glassy) carbon from various manufacturers, polymethyl methacrylate (lucite), bisallyl diglycol carbonate (CR-39, a high quality optical plastic), and diamond.

The exposure obtained during the STS-8 mission was ideal from the point of view of the materials experiment in that about 95% of the atom fluence was accumulated while the vehicle attitude was held so that the ambient atom beam was within 1° of the normal to the material surfaces. The rest of the mission was spent at much higher altitudes or with the payload bay doors closed. Pertinent exposure data are shown in Table 1.

Table 1. STS-8 ATOMIC OXYGEN EXPOSURE DATA

Payload bay forward facing:	t = 41.2 hrs.
Altitude:	120 nautical mi. (225 km)
Velocity:	7.8 km s^{-1}
Mean oxygen atom density (calculated):	2.65×10^9 cm^{-3}
Surface impact frequency:	2.07×10^{15} cm^{-2} s^{-1}
Integral fluence:	3.5×10^{20} atoms cm^{-2}

Erosion observed by this experiment ranged from a thousand angstroms for diamond (which appears to be particularly resistant to oxidation under these conditions), to about 200,000 Å for the polycarbonate resin, CR-39, which was the most heavily eroded sample reported on any space flight exposure.

The temperature dependence of the oxidative effects was measured by conducting the erosion measurements at three temperatures spanning about 120°C. The Arrhenius activation energy, ΔE, was estimated, assuming:

$$r = A\, e^{-\Delta E}/RT$$

where r is the rate of the reaction and A is a constant assumed independent of temperature T. These studies were performed for six materials, vitreous carbon, two graphites, CR-39, silver, and osmium. All activation energies were small and positive.

Results

The conclusions from the measurements on various forms of carbon exposed in the STS-8 mission appear applicable to organic solids in general. They may be summarized as follows:

1. Measured erosion was linear with total fluence.
2. No induction time observed before onset of erosion.
3. Erosion rate linear with oxygen flux (i.e., reaction probability independent of flux) measured over a small range 1.5 to 2.5 x 10^{15} atoms $cm^{-2}\ s^{-1}$.

These results show that erosion and production of gas molecules at the surface can proceed indefinitely at such surfaces as long as oxidizable material remains exposed, in contrast with outgassing behavior which generally shows exponential decay of evolution rate with time. It should be emphasized, however, that our experiment used very pure materials and real or engineering materials may be contaminated either on the surface or by inclusions in the bulk. Such contamination, if less oxidizable than the matrix itself, may then serve to protect the rest of the matrix material from erosion. As erosion proceeds the density of these screening particles or films on the surface grows and the erosion rate may drop from its prior value.

4. Arrhenius activation energies forthe reactions were measured as follows:

Vitreous Carbon	1200 (cal $mole^{-1}$)
Graphite (basal plane)	1400
CR-39	1050

5. Reaction probabilities depend on temperature as shown in (4) above. Reaction probabilities for carbons exposed at ∿300°K ranged from 0.1 to 0.15 where reaction probability equals the number of carbon atoms lost divided by the number of incident oxygen atoms.

6. Reaction probabilities for more complex organic materials have been expressed in cm^3 x 10^{-24} of material lost per incident 0 atom. For present purposes we use two examples at approximately 300° K:

CR-39 $(C_{12}H_{18}O_7)_n$ (this work): ∿6 x 10^{-24} cm^3 $atom^{-1}$

Kapton [Leger et al., 1984]: 3×10^{-24} cm^3 atom^{-1}

Rates of Production of Volatile Species

Our assumption is that the erosion of carbonaceous materials in orbit was caused by the interaction of 5 eV oxygen atoms with a surface of the material, forming volatile products which evaporated into space. We have performed no experiments to measure the nature or composition of the volatile species, and must, therefore, make intelligent guesses. In the case of the pure carbons the range of choice is limited. From the published literature (at higher temperature) the main product is expected to be CO rather than CO_2. The mechanism for this production is not discussed here. In the cases of polymeric films, paints and other solid organic surfaces, the chemistry is likely to be much more complex and quite undefined by experiment. A survey of the experimental data for reactions with commonly used polymers has been given [Leger et al., 1984]. Using the data from 5 and 6 above we may then calculate the emission rates of product molecules from the eroding surfaces in the idealized case. The emitted flux of CO from carbon is given simply by the product of the reaction probability, P, times the flux of oxygen. Calculation of the molecular loss rate from polymers, on the otherhand, requires some assumption of mean molecular weight of the desorbed species.

For the polymers we assumed a mean molecular weight of 28 amu of solid-derived component (i.e., not including the atomospheric component). Since the product mixture may well be complex, and different components will differ radically in their capacity for reactive collision excitation to a glow condition, this level of understanding is clearly inadequate.

For the STS-8 mission, with an oxygen atom flux of 2×10^{15} cm^{-2} s^{-1}, we have:

Substrate	Emitted Species	Rate of Emission (molecules s^{-1} cm^{-2})
Carbon	CO	3×10^{14}
Kapton	(28+) amu	1.9×10^{14}
CR-39	"	3.0×10^{14}

Before these rates are used in any modeling of the gas cloud surrounding the shuttle it should be emphasized that they apply only to unprotected and rather pure organic surfaces. The extent to which impurities reduce the rate of mass loss requires further definition, and it is already quite clear that simple procedures of overcoating with oxidation-resistant materials can reduce mass loss by orders of magnitude. Model calculations of the dynamics of scattering of surface-desorbed species with ambient atmospheric species have suggested that the probability of collision with a streaming oxygen atom is quite high. Under these conditions a large fraction of all organic molecules leaving this shuttle surface may emit one or more photons, contributing to an extended ball of glowing gas around the vehicle, with the upper limit (for 1 mol $\equiv$ 1 photon) for the integral number of photons emitted per second equaling the total number of glow precursors leaving the entire surface per second.

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Fig. 1. One-inch-diameter vitreous carbon disc exposed to the atomic oxygen stream normal to its surface in a 225-km orbit. Rectangles are thin films of niobium. The lighter annulus round the edge of the sample is protected by its holder and remains highly specular, while the inner circle shows the light-absorbing nature of the eroded surface.

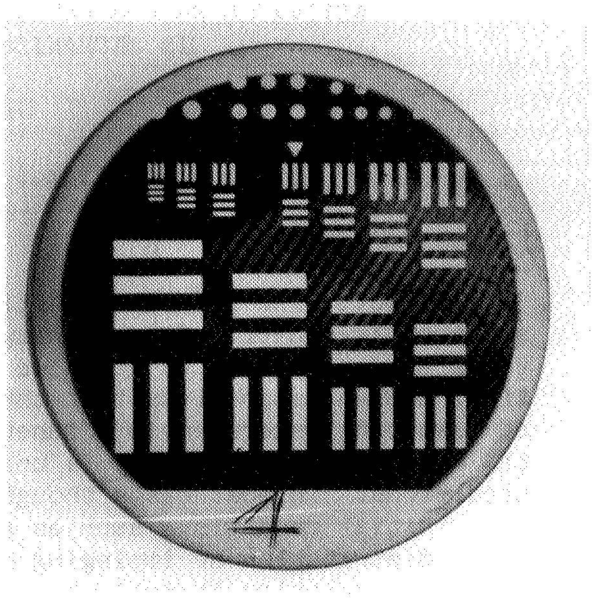

Fig. 2. Scanning electron micrograph of a sample similar to Figure 1 which has been cut through one of the niobium rectangles. Viewing direction is in the plane of the sample. The height of the step (a few µm) indicates the amount of carbon eroded.