Center: Consortium for Materials Development in Space
          The University of Alabama in Huntsville (UAH)

Project Name: **"Materials Preparation and Longevity in Hyperthermal Atomic Oxygen"**

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Annual Report: September 15, 1986 to September 14, 1987

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Introduction

This report includes work on the following tasks:

* Flight Hardware Fabrication

    EOIM-3

* Design and Fabrication of Atom Beam Source

* Construction of Surface Science Laboratory

* Progress in research on processes and mechanisms of interaction of

    hyperthermal atoms at solid surfaces.

* Publications since October 1986

Preparation of Flight Hardware

EOIM-3

Substrates: LiF and graphite single crystals have been purchased. Vitreous
carbon discs were cut and polished during the previous quarter and preparation
of additional samples continues. These surfaces will shortly be characterized
using stylus profilometry and polarizing microscopy.

Silver Detectors: Fifteen CR-39 detector strips were purchased, cut to fit the UAH Scatterometers and coated with Ag using the MSFC RF sputtering facility. These surfaces will shortly be characterized using scanning microdensitometry.

Thermal Atom Beam Facility

The thermal energy oxygen atom beam facility is designed to complement, not duplicate, the much more expensive 5eV atom beams under development at MMDA and elsewhere. It will provide a quantitative basis of comparison with data from these other more energetic sources and from space. The use of discharge "ashers" as oxygen atom sources is quite inadequate for quantitative research necessary to understand the basic reaction mechanisms. The system is designed to provide a known flux of oxygen atoms in the range $10^{14} - 10^{15}$ atoms/cm^2/sec to a target surface maintained in vacua in the 10^{-7} torr range. Using proven designs allows us to have a usable beam at the lowest possible development cost. The design was based on concepts used in several laboratories, including Aerospace Corporation[1] (see also ref. 2 and 3).

The facility is presently under construction. The two major elements of the three-chambered differentially pumped molecular beam apparatus (which may be later adapted to a four-chamber design) consist of a microwave discharge source for the production of an intense beam of atomic oxygen, and a target chamber for reaction studies and beam characterization.

Figure 1 shows a schematic representation of the molecular beam apparatus. The three chambers will be differentially pumped by turbomolecular, ion and cryogenic pumps respectively. Due to the pumping capacity of the turbomolecular pump in the source chamber (chamber 1) sufficient removal of molecular oxygen should occur such that a cryogenic pump can be safely assigned to the sample
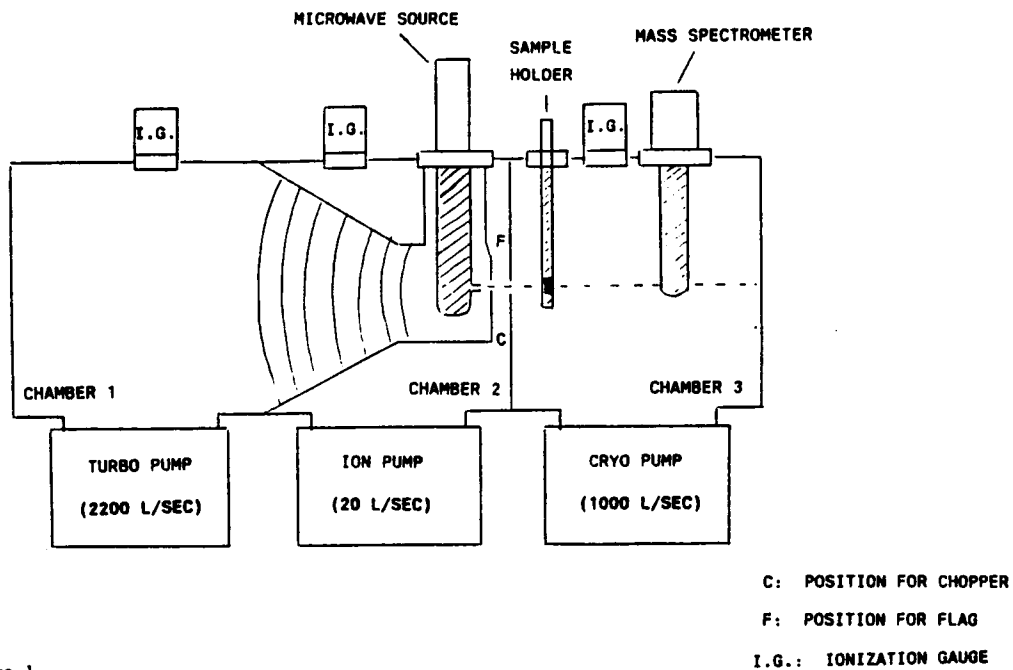
MICROWAVE SOURCE   MASS SPECTROMETER

SAMPLE HOLDER

CHAMBER 1   CHAMBER 2   CHAMBER 3

TURBO PUMP (2200 L/SEC)   ION PUMP (20 L/SEC)   CRYO PUMP (1000 L/SEC)

C: POSITION FOR CHOPPER
F: POSITION FOR FLAG
I.G.:   IONIZATION GAUGE

Figure 1.

ATOMIC OXYGEN FACILITY

Rate = A exp $(\frac{-\Delta E}{RT})$

(a) ΔE = 1440 cal mole^{-1}

(b) ΔE = 1200 cal mole^{-1}

(b) vitreous carbon

(a) single crystal graphite

ln [Reaction Rate] (Arb. units)

100°C   0°C

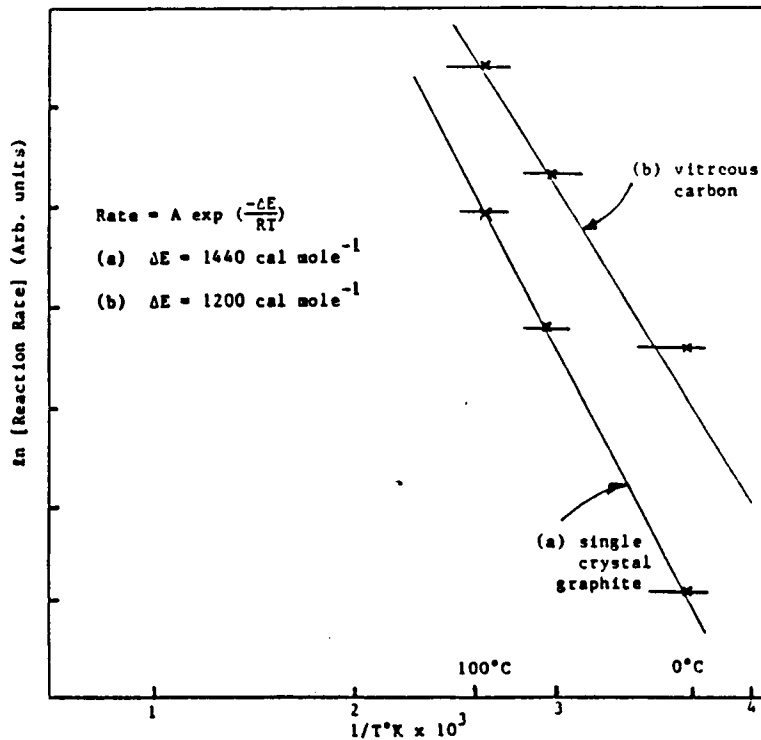1   2   3   4

$1/T°K \times 10^3$

Figure 2.   Arrhenius Plots for Carbon Oxidation by 5eV Oxygen Atoms (STS-8 data)

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chamber (chamber 3). Chamber 2 acts as a collimating chamber, and will also contain beam chopping and flag facilities for the characterization of beams produced. Figure 1 shows the extent to which chamber 1 will be extended into chamber 2. This is to ensure the smallest separation between the microwave discharge source exit orifice and the sample to be exposed, to minimize beam divergence effects. This separation will be approximately 6-8 inches.

The vacuum system is to be based on a 12" diameter stainless steel tubing design, with internal divisions to separate individual chambers. Materials are currently being purchased. Appendage pumping and other chamber accessories are awaiting delivery.

A substantial part of the microwave discharge source has been constructed, the predominant material used being brass. Oxygen atoms will be produced by inducing a microwave discharge in a gas mixture containing O_2. The beam source employs a cavity very similar to that described by Murphy and Brophy.[2] The cavity is a $3\frac{1}{4}$ wave foreshortened coaxial type, with microwave power coupling and cavity tuning of the Evenson design.[3] Power will be supplied to the cavity by a Raytheon PGM-10 2450-MHz magnetron power supply. The discharge tube is of fused silica, 6 mm in diameter with an exit orifice diameter of 1.0 mm.

Progress in Construction of the Surface Characterization Laboratory

Although not funded under the CMDS project, the surface characterization equipment to be installed in this facility is central to the surface research planned for the Consortium year 1987/88. A Perkin-Elmer PH1-5400 small-spot x-ray photoelectron spectrometer has been delivered and a Kratos X-SAM-800 Scanning Auger Spectrometer has been ordered. Contracts for renovation of the building space are well under way. We expect to have our first XPS spectra of surfaces exposed to atomic oxygen soon.

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Progress in Research on Processes and Mechanisms of Interaction of Hyperthermal Atoms at Surfaces

We have previously described our experiment on the STS-8 mission on which the first kinetic data and scattering studies of 5eV O atoms were obtained.

The conclusions form 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 was 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 $cm^{-2}s^{-1}$.

Our experiments used very pure materials, but standard 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. Such protection may result in erosion measurements and derived rates considerably less than those for pure or unprotected material. We have shown that thin films of silicone deposited in space were converted to a layer of SiO_2 2 to 3 nm thick by the ambient oxygen atoms. This film, which overlaid a carbon surface, provided protection from attack by oxygen atoms.

The temperature-dependent rate data for CR-39 were as follows:

Temperature °C	0-20	65	115
Erosion (nm)	22,600	25,000	29,000

Similar data were obtained for the other substrates. Arrhenius activation energies (see figure 2) for some of these were calculated to be:

Material	E (cal mol^{-1})
CR-39	650
vitreous carbon	1200
graphite (basal plane)	1400

These values are quite consistent with literature values of activation energies of $O(^3P)$ with some organic compounds in the gas phase.

While reaction probabilities for carbon surfaces may be simply expressed in terms of C atoms lost per incident O atom (we have measured such probabilities with 5eV oxygen in the range 0.1 to 0.15 atoms per atom), for more complex substrates, reaction probabilities have been expressed in cm^3 x 10^{-24} of material lost per incident O atom. Probabilities for some polymer films were summarized by Leger et al.[4]

Typical values were, at about 300°K (in the units cm^3) x (10^{-24} atom^{-1}) as follows:

CR-39 ($C_{12}H_{18}O_7)_n$ (this work)	6.0
Kapton (an aromatic imide) (ref. 4)	3.0
PMMA (this work)	4.8

Discussion

Comprehensive reviews of atomic oxygen reactions with organic compounds are available.[7,8] It is now well established that the first step of the reaction of $O(^3P)$ with alkanes is abstraction of hydrogen:
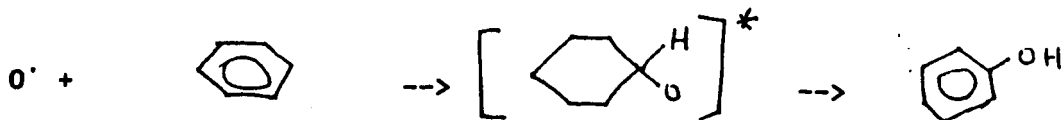
$$RH + O \longrightarrow R\cdot + OH$$
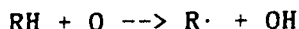
though other possibilities may still occur. In the case of second and further interactions of the same residue with oxygen atoms, however, the picture is very complex and obscure. For the case of surfaces of solid polymers under consideration here, subsequent addition reactions almost certainly occur, but after each addition or abstraction the possibility exists for rearrangement and loss of a volatile fragment.

Reactions with halo alkanes proceed via abstraction of available hydrogen since abstraction of halogen is too endothermic, at least in the case of thermal energy O(3P). This may not be the case for 5eV oxygen atoms, though polyfluorinated hydrocarbons are clearly less reactive in the space environment. Reaction with completely halogenated hydrocarbons may also proceed by addition mechanisms[9], which may be facilitated by a kinetic energy of 5eV. The massive erosion of fluorinated polyethylene observed on materials returned from the solar maximum repair mission was a surprise. The result has been interpreted in terms of the hydrogenated fraction of the material. The reaction rate of fully fluorinated polymers with 5eV oxygen atoms remains unquantified.

For alkenes and alkynes O(3P) adds to the unsaturated bond forming either stable products or rearranging and fragmenting. The relative frequency of these processes depends on the ability of the molecule to accommodate the excess energy according to Cvetanovic[10]. This ability is high in the case of surface reactions, but the behavior with 5eV atoms is quite uninvestigated.

Reactions of O(3P) with aromatic compounds is the least well understood. Oxygen atoms may add to a carbon atom in benzene forming a radical which may rearrange to give phenol:

$$O\cdot \; + \; \bigcirc \;\longrightarrow\; \left[\bigcirc\!\!\!<\!\!\begin{smallmatrix}H\\O\end{smallmatrix} \right]^{*} \;\longrightarrow\; \bigcirc\!\!-OH$$

If a free radical remains in the surface after the first atom reaction, then reaction may occur with another atom. Since the atom-arrival rate of oxygen atoms in low earth orbit is about 1 per surface atom per second, the radical lifetime must be at least this long. Laboratory data on atom-radical reactions is sparse with a considerable amount of data available only for methyl radical reactions. There is however much published information on decomposition pathways of radicals, including those containing oxygen, and these allow deductions to be made on probable reaction paths.

$$O\cdot \; + \; R\cdot \;\longrightarrow\; [RO\cdot]^{*} \;\longrightarrow\; products$$

As Huie and Herron point out, however, even in the case of thermal $O(^3P)$ the produced radicals are most probably excited and other pathways become energetically possible.

The situation is further complicated in the present case if 5eV kinetic energy is available (though this may not be the case; see conclusion below). Also there is a greatly increased possibility of de-excitation of various species at the solid surface. Thus, although a good deal of data exists on reaction path ways of free-radicals with oxygen atoms, the number of possibilities for reaction with polymeric surfaces is so large that elucidation of actual reaction pathways needs experimental measurement _in situ_ of chemical species present on the surface and mass spectrometric measurement of product composition and energy.
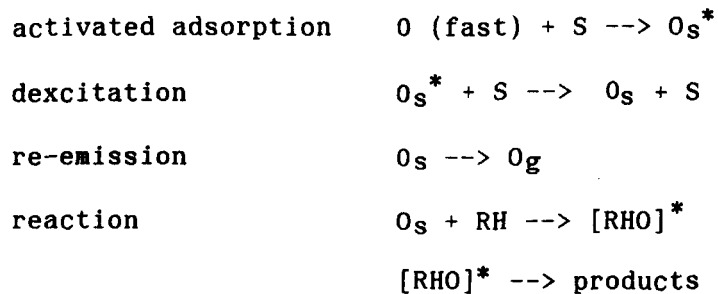
A number of general conclusions can be drawn from the extensive literature on rates of reaction with $O(^3P)$. Some of these are:

- The attack of $O(^3P)$ on carbon compounds is electrophilic in nature.
- For alkanes, secondary hydrogen atoms are 10 to 20 times more likely to be abstracted than primary hydrogen atoms.
- Results for $O(^3P)$ reactions with substituted benzenes shows this electrophilic nature, rate constants varying 2 orders of magnitude from $C_6H_3(CH_3)_3$ to C_6H_5F and $C_6H_5CF_3$.

These conclusions are modified in the case of $O(^1D)$ reactions and may also not be valid with 5eV $O(^3P)$.

Conclusions

Activation energies have been measured for 5eV $O(^3P)$ reactions with solid polymer and carbon surfaces in orbit in the range 4-7 kJ mole^{-1}. These are similar in magnitude to those observed in a variety of reactions of thermal $O(^3P)$ with organic compounds. This fact would be consistent with a model in which the rate-controlling step in the reactions of 5eV oxygen atoms with solid organic surfaces actually involved thermalized O atoms bound at the surface, perhaps in a mobile precursor state. This is also consistent with a measurement of the angular distribution of 5eV oxygen atoms scattered from a carbon surface[11], which showed almost (but not quite) complete energy accommodation. The present authors have also shown, however, that the absolute rate of the reaction of 5eV atoms with carbon surfaces is several times that of thermal atoms. This dependency of rate on kinetic energy only applied, according to this model, to the adsorption step of oxygen into the precursor state. The actual reaction with the organic moiety in the surface to form products may not need to consider the inclusion of 5eV of excitation energy that has already been dissipated. The following reaction sequence is postulated:

activated adsorption	$O \text{ (fast)} + S \longrightarrow O_S{}^*$
dexcitation	$O_S{}^* + S \longrightarrow O_S + S$
re-emission	$O_S \longrightarrow O_g$
reaction	$O_S + RH \longrightarrow [RHO]^*$
	$[RHO]^* \longrightarrow \text{products}$

This conclusion means that the extensive data on thermal $O(^3P)$ reactions may be useful (in so far as gas-phase reactions may be correlated with surface reactions) in interpreting surface reactions of $O(^3P)$ at 5eV.

It should be noted that this does not apply to gas-phase reactions of oxygen atoms with molecules surrounding the Shuttle Orbiter which have been postulated to give rise to the extended Shuttle glow[12]. In this case, intermediates and products will be produced in high energy electronic and vibrational states.

In the final quarter several samples from the space flight STS-8 were analyzed in the newly commissioned UAH x-ray photoelectron spectrometer. Materials investigated were copper, iridium and polymethyl methacrylate. This work is continuing and will be disc   ed in the next quarterly report.

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Publications (Since October 1986)

a. Journal Articles and Published Proceedings

1. "A Measurement of the Angular Distribution of 5eV Atomic Oxygen Scattered off a Solid Surface in Earth Orbit", J. C. Gregory and P. N. Peters, Rarefied Gas Dynamics 15, 644, (1986).

2. "Free Molecule Lift and Drag Deduced from Shuttle Flight Experiment", G. R. Karr, J. C. Gregory and P. N. Peters, Rarefied Gas Dynamics 15, 604, (1986).

3. "Reaction of 5eV Oxygen Atoms with Polymeric and Carbon Surfaces in Earth Orbit", J. C. Gregory and P. N. Peters, Polymer Preprints, accepted for publication, April (1987).

4. "Interaction of Hyperthermal Atoms on Surfaces in Orbit: The University of Alabama Experiment", J. C. Gregory, invited paper in Proc. of the NASA Workshop on Atomic Oxygen Effects, Jet Propulsion Laboratory, Pasadena CA, Nov. 10-12, (1986).

5. "Oxygen Atom Velocity Distributions as Viewed from a Spacecraft and Their Use to Determine Thermospheric Temperatures", P. N. Peters, R. C. Sisk and J. C. Gregory, Journal of Spacecraft and Rockets, (1987), accepted for publication, November (1986).

b. Presentations

1. NASA Workshop on Atomic Oxygen Effects, JPL Pasadena, Nov 10-12, 1986.

2. American Chemical Society Annual Meeting, August-September 1987, New Orleans.

3. European Conference on Application of Surface and Interface Analysis, Stuttgart, October 1987 (Two abstracts submitted.).