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CONF-870507--1

BNL--39712

DE87 010057

Hot Oxygen Atoms: Their Generation and Chemistry

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Only in recent years have studies in hot oxygen atom chemistry begun to be recognized for their fundamental importance to understanding the complex chemistry occurring as a consequence of energy transfer effected through chemical and radiative pathways in numerous photochemical processes [1], and to understanding the complex chemistry involved in combustion [2]. Practical concerns have also been expressed within the aerospace industry over hot oxygen atom initiated surface damage sustained by vehicles as a consequence of their high impact velocity in low earth orbits [3]. Hot oxygen atom chemistry, whether its in the gas-phase or on surfaces, is a poorly understood area because fundamental studies using conventional nucleogenic methods are difficult, if not impossible, to carry out due to the extremely short half-life of the atom's principal radioactive isotope. Molecular beam techniques utilizing supersonic expansion [4] have successfully allowed investigators to probe reaction dynamics of these species at energies below 1 eV. Unfortunately, alternative non-nucleogenic techniques for generating and investigating the chemistry of these atoms at energies between 1 and 10 eV have not been exploited. Such an alternative approach for generating macroscopic concentrations of atomic oxygen in this energy range is presently under development at BNL. These atoms are generated through ion beam sputtering from metal oxide targets. Similar techniques have been shown to generate hot carbon atoms from graphite targets [5].

Source Characteristics

A schematic of the system is presented in Figure 1. The system involves a modification of the existing BNL mass separator belonging to the mass spectrometry group. Positive rare gas ions generated within a dual plasmatron source, are accelerated to voltages between 5 and 60 KeV, and are then focussed into a beam that is subjected to a uniform magnetic field applied by a 90°, 150 cm magnet for momentum analysis. Typically, a 40 KeV argon ion beam can be extracted from the magnetic sector, and focussed into the target chamber at intensities from 15 to 25 μA. Metal oxide targets placed at 60° incident to the path of this beam can be rotated on-axis to provide fresh target surfaces. Gases introduced into the surrounding chamber provide the substrate with which the sputtered atoms react. On-line mass analysis and subsequent GC/MS analysis of gases extracted from the chamber provide information on the structure and stereochemistry of the reaction products.

Studies were carried out to determine the electronic state distribution of atomic oxygen through ion sputtering. It is well-documented that ^1D oxygen atoms undergo reaction with saturated hydrocarbons via C-H insertion to yield the respective alcohol [6], while ground-state ^3P oxygen atoms only abstract H-atoms to yield water. It was possible to measure the metastable state distribution through measurement of alcohol and water yields arising from the sputtered atom's reaction with a saturated hydrocarbon molecule. In test studies, Ta_2O_5 and V_2O_5 targets yielded relatively clean sources of ground-state ^3P atomic oxygen (> 99%). Sputtering yields were also determined from these measurements. The two targets yielded 75 and 190 oxygen atoms per ion impact, respectively, using a 40 KeV argon ion beam. With a 25 μA beam, atom fluxes on the order of 10^{16} atoms cm^{-2} s^{-1} are possible. Higher fluxes can be obtained through the increased sputtering yields possible by using other metal oxide targets. Increasing the mass and energy of the ion beam is also an alternative route [7].

DISCLAIMER

Preliminary measurements were taken on the atom's kinetic energy distribution using a quadrupole mass analyzer modified to house an electrostatic energy filter. In operation, fast neutral atoms were ionized, energy filtered, then mass filtered. Comparisons made between m/e = 16 signals with the ionizer on and off provided a measure of the ion-neutral distribution. Results showed that the ions accounted for only a very small fraction (< 1%) of the sputtered material. It was also noted that the m/e signal ratio 16:181 was stoichiometric for Ta_2O_5 suggesting that the sputtered material is dominantly atomic. Energy distributions measured at both forward (150°) and back scattered (30°) angles on Ta_2O_5 showed energy peaks at ca 7 eV. The distribution at the forward angle was much narrower, and also outweighed the backscattered signal by a factor of 6. Additional measurements on V_2O_5 yielded a bimodal distribution with the lower energy peak at ca 5 eV. These results suggest that some control may be affected over the atom's kinetic energy by altering the nature of the target oxide. In any event, moderating gases can be added to the chamber, as performed in classical hot atom studies, to lower the atom's energy.

Reactions of Hot $O(^3P)$ with Alkenes

Both mechanistic and kinetic aspects of $O(^3P)$ addition to alkenes in the gas-phase have been extensively investigated over the last three decades. Largely through the pioneering work of Cvetanovic [6,8], we've come to realize that while the chemistry of these species seems complex at first sight, there is a predictable nature to their reactions at room temperature and at normal laboratory pressures (as in flow-tube experiments). Under such experimental conditions, $O(^3P)$ atoms will undergo dominant, if not exclusive, addition to carbon-carbon double bonds. Abstraction of a hydrogen atom is, at best, minor under these circumstances, although it has long been assumed to become more important at higher collision energies. Oxygen atom insertion into a C-H bond has only been observed for the ^1D state. The addition reaction is non-stereospecific and presumably yields an excited triplet biradical intermediate. This intermediate will either decompose or, in the presence of collisions involving triplet-singlet conversions, yield hot epoxide and carbonyl products through ring closure and internal rearrangements. However, in the absence of sufficient stabilizing collisions, these hot products will also decompose.

While a strong foundation exists that allows us, in many instances, to predict the nature, yield, and rate of final product formation in bulk experiments, the fundamental aspects of the primary atom-molecule encounter still remain clouded. Researchers such as Lee have attempted to delineate these aspects through reactive scattering experiments performed under single-collision conditions [9]. Studies on simple alkenes have shown that in many instances, the prevention of intersystem crossing through lack of secondary collisions leaves the triplet biradical with no stabilizing channels. Theoretical treatments of internal rearrangements on the triplet manifold support potential barriers that greatly exceed the chemical and kinetic energies that can be imparted to the intermediates internal degrees of freedom [10,11]. On the other hand, these barriers are greatly reduced for the singlet manifold thereby allowing for stabilizing pathways to become more energetically accessible in high pressure reactions.

These aspects have prompted our recent low pressure investigations on hot O(^{3}P) reaction with cis- and trans-butenes. Use of the sputtering source coupled with the ability to moderate kinetic energy through rare gas diluents, allowed us to investigate not only the nature of the primary reaction, but also the degree of internal rearrangement at collision energies extending from room temperature into the high energy regime ($<$ 10 eV). These studies were performed over a 3000-fold range of chamber pressure from 1×10^{-5} to 3×10^{-2} Torr. Information obtained through GC-MS and on-line MS provided distributions for stabilization (S), decomposition (D) and H-abstraction (A) pathways. Table I presents a sampling of such data obtained from moderated trans-butene and unmoderated cis-butene studies carried out at constant chamber pressure. The last column depicts the branching ratio between π-bond addition and H-abstraction channels. Results indicate that the abstraction channel is indeed minor at thermal energy, however, it actually dominates the high-energy regime. Additional scrutiny of this ratio, in a comparison between unmoderated trans- and cis-butenes also shows a stereochemical effect where the trans-isomer is more susceptible to H-abstraction than the cis-isomer. In fact, this phenomena is observed throughout the entire accessible pressure range. Part of this effect may be the result of greater internal excitation of the trans biradical yielding greater decomposition. A smaller S/D value is indeed observed with the trans-isomer, but it is not sufficient to account for the magnitude of the difference in the reactive branching ratio. This suggests that a stereochemical effect may be exerted at the point of the atom's approach to the molecule thereby altering its effectiveness for abstraction.

Delineation of certain aspects of the energy transfer pathways in the isomeric biradicals can also be made by comparing distributions of isomeric products between cis- and trans-butenes. Stabilized products fit into two categories: (1) those possessing the formula C_4H_8O which were identified as butanone, cis- and trans-epoxides and 3-buten-2-ol; and (2) those possessing the formula C_4H_6O which were identified as 3-butenone and isobutenal. Products requiring internal rearrangement, such as butanone from 1,2-H-migration and isobutenal from 1,2 methyl-migration were observed in higher yields in trans-butene supporting enhanced vibrational excitation in the trans biradical. Likewise, a greater degree of non-selective addition forming the cis-epoxide product was observed in low pressure trans-butene studies, suggesting enhanced rotational excitation. It remains to be seen whether the observed differences in biradical stabilities can be linked to fundamental differences in the way hot $O(^3P)$ adds to cis- and trans-butenes.

This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.

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Figure Captions

Fig. 1 Schematic of ion sputtering hot $O(^3P)$ atom system.

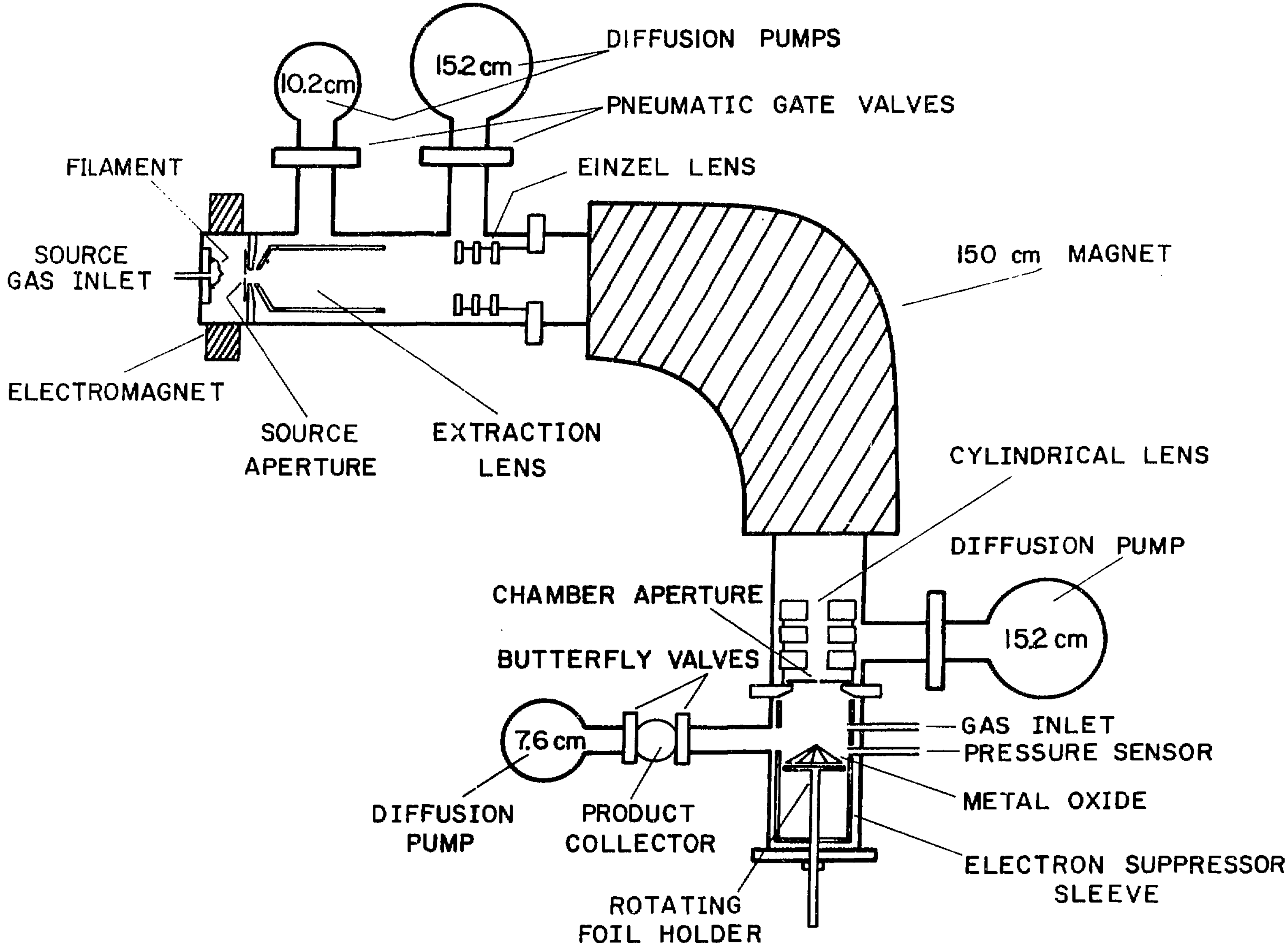
DIFFUSION PUMPS
10.2 cm
15.2 cm
PNEUMATIC GATE VALVES
FILAMENT
EINZEL LENS
SOURCE
GAS INLET
150 cm MAGNET
ELECTROMAGNET
SOURCE
APERTURE
EXTRACTION
LENS
CYLINDRICAL LENS
DIFFUSION PUMP
CHAMBER APERTURE
15.2 cm
BUTTERFLY VALVES
7.6 cm
GAS INLET
PRESSURE SENSOR
METAL OXIDE
DIFFUSION
PUMP
PRODUCT
COLLECTOR
ELECTRON SUPPRESSOR
SLEEVE
ROTATING
FOIL HOLDER

Table 1

Substrate	% Neon	S/(A+D)[a,b]	A/D[c]	S/D	(S+D)/A
t-2-Butene	0	0.09	3.30	0.38	0.42
"	80	0.20	1.05	0.41	1.36
"	98	0.37	0.06	0.39	24.92
c-2-Butene	0	0.38	0.50	0.57	2.14

a. (S) represents stabilization products comprising C_3O and C_4O products. (D) represents complete decomposition to CO. (A) represents hydrogen atom abstraction channel yielding hydroxyl radical.

b. (S/(A+D)) ratios were obtained from GC-MS analysis of products.

c. (A/D) ratios were obtained from on-line mass analyses of m/e signals at 18 and 28 corresponding to H_2O and CO yields. The abstraction channel was also corrected for hydroxyl radical addition to butene yielding alcohol products.