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OXYGEN RADIOLYSIS BY MODULATED MOLECULAR BEAM MASS SPECTROMETRY

by

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ABSTRACT

An experimental system for on-line mass spectrometric analysis of gas phase radiolysis systems was developed. Oxygen in a fast flow reaction tube was irradiated with 1 MeV protons and subsequently sampled with a molecular beam source. Analysis of the modulated molecular beam with a quadrupole mass spectrometer provided the concentrations of O, O₂, and O₃ as functions of reaction time, dose rate, and system pressure. Observed ozone levels were anomalously high compared to the predictions of existing chemical models, with apparent g-values considerably above theoretical maximum values. Agreement of theory with the data was improved by postulating an excited state of O₂ as a direct precursor to ozone.

I. INTRODUCTION

Ideally, a complete description of the interaction of high energy radiation with a gas should identify all chemical species produced, determine the production efficiency for each, and consider the kinetics of all subsequent chemical reactions which ultimately lead to stable products. Oxygen radiolysis, in which the sole stable product is ozone, is interesting for several reasons. First, the action of high energy protons on low pressure oxygen, which is the subject of the present study, simulates the effect of solar flare protons on the upper atmosphere. Second, the process has potential application in chemonuclear ozone production^(1,2). Third, oxygen radiolysis is especially simple for experiments utilizing on-line mass spectrometry, since only three species, O, O₂, and O₃, are observable in the mass spectrum. Finally, the rate constants of many of the homogeneous reactions involved in the overall process are well known, so that the unknown aspects of the radiolysis can be singled out for study.

Although oxygen radiolysis has been studied previously, the experiment described here differs in several respects from earlier experiments⁽³⁻⁹⁾. In the present system, atomic oxygen is measured in addition to ozone. Both products are observed on-line simultaneous with irradiation. The chemical reactions take place concurrent with irradiation rather than afterwards, as in pulse radiolysis.

II. EXPERIMENTAL DESCRIPTION

The quantities measured are the concentrations of atomic oxygen and ozone, as functions of gas pressure, gas flowrate, and proton beam intensity. The apparatus shown in Fig. 1 can be divided broadly into three systems: (A) equipment for production and measurement of the proton beam; (B) the reaction tube and the flow system; (C) mass spectrometer for identification and quantitative measurement of the radiolysis products.

A. Production and Measurement of the Proton Beam

The primary proton beam is produced by a 1 MeV Van de Graaff accelerator. The protons are deflected into the reaction tube by a bending magnet, which produces a mono-energetic beam.

One of the major problems in this work was to devise a method of introducing the proton beam into the reaction tube, where the gas pressure is several torr, from the accelerator tube where the pressure is 10^{-6} torr. Thin windows of aluminum, beryllium, carbon, and formovar were tested but these failed quickly because of localized heating by the proton beam and attack of the hot spot by the reactant gas. Eventually, the differential pumping system shown in the lower left hand corner of Fig. 1 was developed. Two channels (or collimators) 2.5 mm in diameter and 10 cm long separate the reaction tube from the accelerator. Each collimator is followed by a vacuum pump. The basic idea was to sufficiently restrict the flow of the randomly moving reactant gas into the accelerator so as not to exceed allowable pressures there yet at the same time not lose too much of the incident proton beam on the collimators. The collimator system which was devised satisfies the following criteria: (1) the pressure rise in the accelerator tube during the operation with 10 torr gas pressure in the reaction tube is approximately 10^{-6} torr; (2) the fraction of the total gas flow in the reaction tube which is pumped

off by the collimator system is small ($<1/3$); (3) not too large a fraction of the available proton beam is lost because of the twin collimator system. The maximum proton current obtainable in the reaction tube is $\sim 3 \mu\text{a}$ at 0.9 MeV, which represents an order of magnitude loss in available beam.

The proton current at the far end of the reaction tube cannot be measured during the experiments by a standard Faraday cup because the ions produced in the gas are collected and result in large, spurious currents. To surmount this problem, a modified Faraday cup was constructed. The proton beam is stopped in a thick tantalum foil (45 mg/cm^2) and the tantalum K X-rays produced by the interaction are monitored by a lead-shielded Ge(Li) detector. The output of the detector is amplified, fed to a ratemeter and recorded. The proton detection system was calibrated by simultaneous measurement of the ratemeter output and the proton beam current (the Faraday cup was biased to prevent escape of secondary electrons) with the reaction tube under vacuum. When gas is admitted to the reaction tube, there is a noticeable decrease in the detector output, due to either: (1) decrease in the X-ray yield per proton because of proton energy loss in the gas, or (2) loss of protons to the walls of the reaction tube by angular deflections resulting from the atomic collisions occurring between the beam and the gas. Knowing the variation of the tantalum K X-ray yield with proton energy and the stopping power of protons in oxygen as a function of gas pressure, the decrease in detector response with increasing

gas pressure could be predicted. This prediction was in reasonably good agreement with the observed behavior of the detection system so that proton loss due to scattering by the gas is probably not significant in our experiments. A calculation shows that the rms radial displacement of the protons from the beam axis due to Rutherford collisions with the oxygen atoms is ~ 0.3 mm at the end of the reaction tube⁽¹⁰⁾.

B. Reaction Tube and Flow System

The reaction tube shown in Fig. 2 is fabricated of pyrex and treated with phosphoric acid to reduce wall recombination of atomic oxygen⁽¹¹⁾. The irradiated section is 1.56 cm inside diameter and 57 cm long. The second section provides the vertical offset required by the different elevations of the accelerator beam tube and the mass spectrometer detection equipment. The molecular beam sampling source is located at the end of a third, horizontal section. A pressure tap is placed at the downstream end of the irradiated section. The system is pumped by a liquid nitrogen-trapped 70 cfm mechanical pump. The pressure drop and mean gas velocity are calculated from laminar flow theory. Under normal experimental conditions, the pressure in the reaction tube is a few torr and the gas velocity is 0.2 - 0.5 m/sec. Research grade oxygen (99.95% purity) is used without further treatment. All intermediate lines and fittings in the oxygen supply system are fabricated of cleaned and baked stainless steel. No water vapor is detected mass spectrometrically in the gas (detection limit ~ 2 ppm).

C. Mass Spectrometer Detection System

The mass spectrometer detection system shown on the right hand side of Fig. 1 is described in detail elsewhere⁽¹²⁾. It consists of a molecular beam source for sampling the gas flowing through the reaction tube, a roughing chamber which contains a mechanical chopper for modulating the molecular beam effusing from the source, and an ion pumped chamber where the quadrupole mass spectrometer is housed. These two vacuum chambers are separated by a 1 mm diameter aperture, which serves to pass a well-collimated molecular beam of about 3 mm diameter directly through the ionizer of the mass spectrometer. With a pressure of 2.5 torr in the reaction tube, the pressures in the roughing and mass spectrometer chambers are 3×10^{-6} and 2×10^{-8} torr, respectively. As a result of the signal-to-noise reduction afforded by mechanical chopping of the molecular beam and lockin amplification of the mass spectrometer output signals, concentrations as low as 2 ppm in the bulk oxygen gas can be quantitatively detected⁽¹²⁾.

The molecular beam source used for sampling the reacting gas mixture consists of an array of ~5000 channels, each 11 μm in diameter and 0.25 cm long, packed into a 1 mm² area. The characteristics of this source and of the molecular beam it produces are reported elsewhere (ref. 13, the "Mosiatic A" source). The extent of oxygen atom recombination due to wall collisions in the channels of the source was determined from kinetic theory⁽¹⁰⁾. Using a wall recombination coefficient of 10^{-4} , a 7% loss in atomic oxygen in the sampling process is calculated.

In order to measure the atomic oxygen content of the reacting gas mixture, the mass spectrometer must be calibrated. Let $[O]$ and $[O_2]$ be the concentrations (in particles/cm³) of oxygen atoms and molecules, respectively, at the molecular beam source position in the reaction tube. The flux of either of these species through the molecular beam sampling source is proportional to the product of the concentration and the mean molecular velocity. The mass spectrometer is operated as a density sensitive detector, and provides an output signal which is proportional to the density of particles in the ionizer. The concentration at this point is proportional to the flux issuing from the molecular beam source divided by the mean molecular velocity. Consequently, in the absence of wall recombination in the molecular beam source, the density of a particular species in the ionizer is proportional to the density of this species in the reaction tube at the sampling point, and the constant of proportionality is independent of the mass of the species detected.

When the ionizing electron energy in the mass spectrometer is adjusted to give the maximum signal (~ 65 eV for most species), substantial fragmentation of O_2 to O^+ occurs. Thus the measured signal at mass 16 (S_{16}) is the sum of contributions due to single ionization of O atoms (denoted by S_O) and dissociative ionization of O_2 . Similarly, the measured mass 32 signal, S_{32} , is less than the signal S_{O_2} which would be measured in the absence of fragmentation. The quantities S_O and S_{O_2} are proportional to the densities of O and O_2 in the ionizer. The constants of proportionality, β_O and

β_{O_2} , depend upon the ionization cross sections, the extraction and transmission efficiencies of the mass spectrometer and on the secondary electron coefficients of the electron multiplier for the atomic and molecular ions. Taking all of the effects cited above into account, the ratio of the O atom and O_2 molecular concentrations in the reaction tube at the position of the molecular beam source is given by:

$$\frac{[O]}{[O_2]} = \frac{1}{0.93} \frac{S_O/\beta_O}{S_{O_2}/\beta_{O_2}} = \frac{1}{0.93} \left(\frac{\beta_{O_2}}{\beta_O} \right) \frac{(S_{16}/S_{32}) - \gamma_{16}^{32}}{1 + \gamma_{16}^{32}} \quad (1)$$

The factor $1/0.93$ accounts for recombination of atomic oxygen on the channel walls of the molecular beam source and γ_{16}^{32} is the cracking fraction of O_2 , defined as the ratio of the signals at mass 16 and mass 32 when pure oxygen is introduced into the ionizer. For our mass spectrometer, $\gamma_{16}^{32} = 0.17$ for 65 eV ionizing electrons. S_{16}/S_{32} is the ratio of the measured mass spectrometer output signals at mass 16 and mass 32.

Calibration of the system for atomic oxygen consists of determining the sensitivity ratio β_{O_2}/β_O from Eq.(1) by means of experiments in which the atomic oxygen concentration in the reaction tube is known. For this purpose, O atoms were produced by placing a microwave discharge unit at an upstream position in the irradiation section of the reaction tube. The concentration of atomic oxygen was measured at three locations downstream from the discharge by NO_2 titration^(11,14) (in the calibration experiments, three inlet ports were added to the long section of the reaction

tube). A short extrapolation of the measured O atom concentrations at these points (which ranged from 3 to 4 atom percent O) yielded the O atom concentration at the molecular beam source. When combined with the measured O₂ pressure in the reaction tube, the left hand side of Eq.(1) was determined. As a result of a number of separate calibration experiments using discharge-produced O atoms, the ratio β_{O_2}/β_O was determined to be 1.0 ± 0.05 for 65 eV ionizing electrons.

During the proton irradiation experiments, the amount of atomic oxygen produced is so small that it cannot be determined in the presence of the mass 16 signal from O₂ fragmentation (i.e., at 65 eV electron energy, S_{16}/S_{32} in Eq.(1) is very nearly equal to γ_{16}^{32} even when radiolysis is going on). The signal due to double ionization of atomic oxygen (at mass 8) was also too small to be reliably extracted from the noise even with lockin amplification. However, the different threshold energies for the various ionization processes in the mass spectrometer provided a means of detecting O atoms. The pertinent reactions and their thresholds are:

There is a window between electron energies of 13.55 eV and 18.73 eV where reaction B is suppressed but reaction C is energetically possible. Consequently, the ratio $[O]/[O_2]$ was determined during the radiolysis experiments by measuring the signal ratio S_{16}/S_{32} at an ionizing electron energy of 17 eV. However, Eq.(1) cannot be used

directly to calculate the concentration ratio from the measured signal ratio (even though γ_{16}^{32} is zero) because the ratio β_{O_2}/β_O is not the same for 17 volt electrons as it is for 65 volt electrons (where this ratio was measured). The primary energy dependent component of β is the ionization cross section of the species bombarded by electrons. To account for the variation of the cross sections with electron energy, the instrumental constants for O and O_2 were both assumed to obey the same functional form, namely:

$$\left(\frac{\beta}{\beta_{65}}\right)_O = \left(\frac{\beta}{\beta_{65}}\right)_{O_2} = K \left(\frac{E - E_0}{65 - E_0}\right)^n \quad (2)$$

where E_0 is the threshold energy for single ionization and β_{65} is the value of β appropriate to an electron energy of 65 eV. Eq. (2) is valid in the range $E_0 \leq E \leq 18$ eV. The constants K and n in Eq. (2) were determined by measuring the increase in the total mass spectrometer signal (O_2^+ and O^+) as a function of electron energy when pure O_2 was introduced into the ionizer. Using the experimentally determined value of $n = 1.5$ and Eq. (2), the ratio of instrumental constants for 17 eV electrons is related to this ratio for 65 eV electrons by:

$$\left(\frac{\beta_{O_2}}{\beta_O}\right)_{17} = \left(\frac{\beta_{O_2}}{\beta_O}\right)_{65} \left(\frac{17 - 12.21}{65 - 12.21}\right)^{1.5} \bigg/ \left(\frac{17 - 13.55}{65 - 13.55}\right)^{1.5} = (1.0)(1.57) = 1.57$$

Thus, the ratio $[O]/[O_2]$ at the molecular beam source during irradiation is equal to 1.57/0.93 times the measured signal ratio S_{16}/S_{32} for 17 eV electron energy in the mass spectrometer ionizer.

The ozone peak at mass 48 is in a low background region of the mass spectrum. During radiolysis this signal was detectable at an electron energy of 65 eV. The analog of Eq.(1) for the ozone-to-oxygen ratio at the molecular beam location in the reaction tube is:

$$\frac{[O_3]}{[O_2]} = \left(\frac{\beta_{O_2}}{\beta_{O_3}} \right) \left(\frac{S_{48}}{S_{32}} \right) \frac{1 + \gamma_{32}^{48} + \gamma_{16}^{48}}{1 + \gamma_{16}^{32}} \quad (3)$$

Fragmentation of both species in the mass spectrometer ionizer is taken into account using the ozone cracking pattern determined by Herron and Schiff⁽¹⁵⁾ ($\gamma_{32}^{48} = 5.0$; $\gamma_{16}^{48} = 0.5$). The ratio of the instrumental constants for 65 eV electrons, β_{O_2}/β_{O_3} , was assumed to be unity because the comparable ratio O/O_2 was found to be very close to one.

III. RESULTS

The measured concentrations of atomic oxygen and ozone at the molecular beam source position in the reaction tube are shown in Figs. 3 and 4 as functions of energy deposition and system pressure. The experimental parameters corresponding to each set of data are given in Table 1. The product concentrations along the ordinates of Figs. 3 and 4 were determined from the mass spectrometer signals using Eqs.(1) and (3). The concentration of molecular oxygen was determined from the system pressure measurement and pressure drop calculation. The total energy deposition in the gas was obtained by integrating the energy deposition rate over irradiation time:

$$E_d = \int_0^{L_1} \dot{E}_d (dx/v)$$

where v is the flow velocity and L_1 is the length of the irradiated section of the reaction tube. The energy deposition rate $\dot{E}_d$ was calculated from the proton current, the oxygen concentration, the cross sectional area of the reaction tube and the stopping power of protons in oxygen⁽¹⁶⁾.

The estimated precision of the quantities plotted in Figs. 3 and 4 are $\pm 25\%$ for the concentrations of atomic oxygen and ozone. The precision of the E_d measurements is estimated to be $\pm 5\%$ at low pressure and high proton beam strength to $\pm 20\%$ at opposite extreme. These uncertainties are due principally to countrate statistics in the beam detection apparatus (Sec. IIA).

IV. COMPARISON OF DATA WITH THEORETICAL MODELS

The oxygen radiolysis system can be analyzed theoretically by solving one-dimensional conservation equations which describe the rate of change of the concentration of each species present with time (or, equivalently, with position, since $dt = dx/v$). For each species i , the conservation statement includes radiolytic production of creation by chemical reaction. Denoting the concentration of species i by $[i]$,

$$\frac{d[i]}{dt} = g_i \dot{E}_d + R_i \quad (4)$$

where R_i is the rate of production of species i by all chemical reactions. g_i is the g -value of species i , or the number of particles of this species produced as a direct result of the deposition of 1 heV (100 eV) of radiolytic energy in the gas.

Two models of the radiolytic process, a full one and a simplified one, were investigated. The full model includes the three primary processes and the 27 subsequent reactions shown in Table 2. Most of the rate constants for the secondary reactions are known. The g-values for the ionic species can be determined from the known W-value for oxygen ($W = 30.9$ eV/ion pair) and the assumption that the ratio of O^+ to O_2^+ is the same as the mass spectrometer cracking fraction, 0.17. The resulting g-values are 2.7 and 0.5 for O_2^+ and O^+ , respectively. The g-value for direct production of O atoms from $O_2(g_0)$ however, is not known for proton bombardment. However, bounds may be placed upon this quantity. The minimum energy required to form the $2.7 + 0.5 = 3.2$ ions per heV of $O_2^+ + O^+$ is 42.6 eV, calculated from the ionization potentials. Assuming that the bond energy of O_2 is 5.12 eV⁽¹⁷⁾ the maximum number of O-atoms which can be produced is $2 \times (100 - 42.6) / 5.12 = 22.4$ atoms/heV. To allow for uncertainty in the cracking fraction and to account for the neutral O atoms formed in dissociative ionization, a conservative upper bound on g_0 is 24 atoms/heV. Similar calculations allowing for more loss processes was carried out by Willis et.al.⁽⁶⁾, and their estimate of g_0 is 7.5. In analyzing oxygen radiolysis by the complete model, the 10 differential equations for the 10 species in Table 2 were solved numerically with g_0 as an adjustable parameter.

The calculation of the chemical response of the system according to the full model described in the preceding paragraph proved to be time consuming even on a large digital computer. A great many runs were required to establish response trends as

each of the experimental parameters was varied. For these reasons, a simplified model was constructed. This model was based upon the full model but was sufficiently streamlined that the differential equations were decoupled and could be solved analytically.

The major assumption required to reduce the full model to the simplified model is that neutralization of each O_2^+ ion, by whatever route, results in the net production of two neutral O-atoms. It is also assumed that O^+ is neutralized by charge transfer to O_2 (Reaction I-1), so that each O^+ ion results in three neutral O-atoms (i.g., one from I-1 and two from I-6). Since the ion reactions occur on a much faster time scale than the neutral reactions, O-atom production via this route appears to enhance the direct production; that is, atomic oxygen is produced as if with an "effective" g-value of:

$$g(O)_{\text{eff}} = g_0 + 2g_{O_2^+} + 3g_{O^+} = g_0 + 6.9 \quad (5)$$

Order-of-magnitude considerations allow neutral reactions N-2, N-4, and N-5 to be neglected relative to N-1 and N-3, and the differential equations for the concentrations of atomic oxygen and ozone are:

$$d[O]/dt = g(O)_{\text{eff}} \dot{E}_d - k_{N1}[O][O_2]^2 - k_{N3}[O] \quad (6)$$

$$d[O_3]/dt = k_{N1}[O][O_2]^2 \quad (7)$$

Equations (6) and (7) can be readily integrated to predict the atomic oxygen and ozone concentrations at the time equivalent to the position of the sampling point in the reaction tube. In the integration, the source term (the first term on the right hand side

of Eq.(6)) is active only over the irradiated section of the reaction tube.

Figures 5 and 6 compare the O and O₃ data at 3.45 torr with the model predictions, and Fig. 7 compares the experimental and theoretical variations of product concentrations with system pressure for $E_d = 2.5 \times 10^{12}$ heV/cm³. Figure 5 shows that a value of $g_0 = 5$ provides good agreement between the experimental dose dependence of the atomic oxygen concentration and the predictions of the simple model. However, the predictions of the full model, which should be more accurate than those of the simple model, suggest that this value of g_0 is too small. Although the simple model with $g_0 = 5$ adequately reproduces the O atom data, it fails by a factor of five to predict the measured O₃ concentrations (Fig. 6). The full model predictions (with $g_0 = 5$) are in even poorer agreement with the ozone data. The comparison shown in Fig. 7 shows that the simple model with $g_0 = 7.5$ (curve A) satisfactorily predicts the pressure dependence of the O atom concentration at high pressures but does not reflect the distinct maximum in [O] at $p_s = 2.5$ torr. The predictions of the full model (curves B and C in Fig. 7) are lower than the data even when the upper bound on g_0 is used (curve B). The bottom graph of Fig. 7 shows the same dramatic underprediction of the ozone concentrations from both model calculations as seen in Fig. 6.

V. DISCUSSION

Before accepting the failure of the theoretical models of the oxygen radiolysis system, the possibility that the discrepancies are due to large systematic experimental errors was explored. Probable systematic errors in the measurement of the proton energy and current, the oxygen flow rate, and the mass spectrometer measurement of $[O]$ and $[O_3]$ were analyzed in detail⁽¹⁰⁾. The most likely error source is the assumption that the mass spectrometer instrumental constant ratio β_{O_3}/β_{O_2} is equal to that measured for atomic oxygen β_{O_2}/β_O . However, examination of the species-dependent components of β (i.e., the ionization cross section and the electron multiplier efficiency) indicate that the observed factor of five discrepancy can not be accounted for in this manner. Neither is use of an ozone fragmentation pattern obtained from the literature subject to such large error, particularly since our observed O_2 cracking fraction is comparable to those measured by other investigators. Additional evidence of the reliability of the ozone measurements came from the O-atom calibration experiments using the microwave discharge apparatus, in which $[O_3]$ was also measured. The ozone concentrations observed in these tests was substantially lower than those predicted by the theoretical models, a phenomenon which Kaufman and Kelso⁽¹⁹⁾ have also observed.

As a result of the error analysis, we have concluded that the discrepancies between the data and existing theoretical models of oxygen radiolysis are real and that the theory needs to be modified. The primary consideration in the formulation of a modified kinetic model is that ozone should be produced very efficiently. Figure 4 shows that the ratio of $[O_3]:E_d$ is in the range 20-40 molecules/heV, or the energy required to produce one ozone molecule is between 2.5 and 5.0 eV. From the discussion of the maximum g_0 value it is clear that mechanisms assuming atomic oxygen as the sole precursor to ozone require a minimum of 4 eV/ozone molecule (maximum $g_0 \sim 24$, one molecule of ozone for each atom of oxygen). Such mechanisms are, therefore, energetically incapable of predicting the bulk of the ozone data. Also, the $[O_3]:[O]$ ratio is determined primarily by the reaction:

and the elapsed reaction time. The rate constant k_{N1} and the measured $[O_3]:[O]$ ratio are quite reliable, and the fact that the latter is substantially higher than the ratio predicted by the models is another indication that ozone is being produced in some more efficient way than via reaction N1.

One simple possibility is an excited state O_2^* , produced directly by the irradiation, which undergoes the subsequent reaction:

This reaction has been postulated by others^(5,21) but has not been discussed in detail. If the contribution to $[O_3]$ from such a reaction were comparable to or greater than that from reaction (N-1),

the resulting $[O_3]:[O]$ ratio would clearly increase. Also, the energetics involved are somewhat more favorable, since reaction (N-*) requires an excitation energy of ~ 4 eV⁽¹⁷⁾ (for a potential maximum of two ozone molecules per O_2^*) as opposed to 5.12 eV for direct O_2 dissociation⁽¹⁷⁾, or ~ 9 eV for dissociative transitions to an unbound $O_2(^2\Sigma_u^+)$ state⁽⁶⁾.

Sample calculations utilizing the simple model with this modification were carried out at $E_d = 2.5 \times 10^{12}$ heV/cm³. Three unknown parameters are required for such calculations: g_0 , $g_{O_2}^*$, and k^* , and the rate equations are:

$$\frac{d[O]}{dt} = (g_0 + 6.9) \dot{E}_d - k_{N1}[O][O_2]^2 - k_{N3}[O] + k^*[O_2^*][O_2] \quad (8)$$

$$\frac{d[O_2^*]}{dt} = g_{O_2}^* \dot{E}_d - k^*[O_2^*][O_2] \quad (9)$$

$$\frac{d[O_3]}{dt} = k_{N1}[O][O_2]^2 + k^*[O_2^*][O_2] \quad (10)$$

The $[O_3]:[O]$ ratio increases as $g_{O_2}^*$ increases relative to g_0 . However, $g_{O_2}^*$ cannot increase indefinitely, since the energetics require an upper limit similar to that calculated previously for g_0 . The maximum $[O_3]:[O]$ ratio occurs with the minimum g_0 value, which can be calculated by assuming that all direct O atom production occurs via dissociative Schumann-Runge transitions and taking the ratio of dissociation to ionization to be approximately the same as the ratio of the cross sections for these two processes, which is ~ 0.1 ^(22,23). The minimum g_0 value is, therefore, taken

as $0.1 \times 2 \times 3.2 \approx 0.6$ O atoms/heV, requiring $(0.6)(9 \text{ eV}) = 5.4 \text{ eV/heV}$ and the energy remaining/heV is slightly over 50 eV (i.e., $100 - 5.4 - 42.6$). Since each O_2^* must have on the order of 4 eV, the maximum value of $g_{O_2}^*$ is roughly 12.5.

An estimate of the rate constant k^* may be obtained from that of the corresponding ground state rate constant ($O_2 + O_2 \rightarrow O_3 + O$), which is available in the literature⁽¹⁸⁾. If it is assumed that the energy carried by the O_2^* molecule affects the rate constant only by reducing the activation energy, the rate constant for the excited O_2^* reaction is of the order $1-10 \text{ (torr-sec)}^{-1}$.

The results of the modified simple model using $k^* = 10 \text{ (Torr-sec)}^{-1}$ ($\sim 3 \times 10^{-16} \text{ cm}^3/\text{molecule-sec}$), $g_O = 0.6 + 0.5 = 1.1$ (contributions from direct dissociation and from dissociative ionization) $g(O)_{\text{eff}} = 8.0$, and $g_{O_2}^* = 12.5$ are shown in Fig. 8. Substantial improvement in the predicted $[O_3]:[O]$ ratio is obtained. This ratio may be brought closer to the data if the full model is used, since the dominant loss mechanism in this model is atomic recombination (reaction N-2 in Table 2) as opposed to ozone decomposition (reaction N-4). However, based upon the trends exhibited by the curves in Figs. 5-7, use of full model calculations would probably lower both concentrations. While the agreement with the $[O]$ data would be improved by incorporation of the postulated O_2^* species and its reactions into the full model, the match with the $[O_3]$ data would be worse than that seen in Fig. 8.

Although the identity of the hypothetical state O_2^* cannot be determined, most of the ~ 4 eV energy is probably in vibrational excitation ($v \sim 21$). An $O_2 - O_2^*$ complex would release an atom of atomic oxygen (dissociate at the vibrationally excited bond). The postulated vibrationally excited state O_2^* could be formed in several possible ways. Interaction between protons and bound electrons in O_2 with less energy transfer than that required for ionization or allowed electronic transitions is one possibility. The objection to this mechanism is that energy transferred to an atomic electron is not readily transformed into nuclear motion within the molecule (i.e., to vibrational excitation). Alternatively, some of the molecules resulting from ion recombination may be in vibrationally excited states; vibrational excitation of the O_2^- ion, for example, can occur at any energy above zero⁽²⁴⁾. This possibility limits the production of the proposed O_2^* species to quantities comparable to the ionization yields, which alone could not account for the observed ozone concentrations.

The proposed mechanism modification is probably only partially responsible for the very high ozone levels observed. The calculated values of $[O]$ and $[O_3]$ are both increased by inclusion of this modification, and the calculated $[O_3]:[O]$ ratio is increased as well. All these changes are in the correct direction. However, the modified model does not provide a full explanation for the discrepancy between theory and experiment. Assuming that a species such as O_2^* is produced, it seems unlikely that sufficient

quantities of it can be produced to account for the observed ozone yields, even allowing for the large uncertainties in the data.

Also, excited O_2 molecules generally decompose ozone rapidly, an effect that has been observed for the two stable electronically excited states ($1\Sigma_g$ and $1\Sigma_g^+$) (17,25,26) and is expected for molecules in high vibrational states⁽¹⁸⁾.

In searching for other explanations for the discrepancy, we noted that the term in the rate equations resulting from the proposed modification is proportional to the system pressure (i.e., to $[O_2]$), whereas the term arising from reaction (N-1) varies as $[O_2]^2$. Since the rate of the O_2^* reaction and that of reaction (N-1) are postulated to be of comparable magnitudes at the pressures used in this experiment (1-5 Torr), one could expect the latter rate to dominate at the higher pressures used by other investigators. Anomalously high ozone levels at low pressures were anticipated by Willis et.al.⁽⁶⁾ as a result of the high yields observed by these investigators in other radiolysis systems. Although such behavior was not found in their investigation of the oxygen system, the lowest pressure they used was 30 Torr, substantially above the pressure range in the present work. The high yields they observed were attributed to acceleration of secondary electrons in transient electric fields which were assumed to result from the very high dose rates and consequently high charge density in their apparatus ("high" dose rates are considered to be $\sim 10^{26}$ - 10^{27} eV/gm-sec^(3,6), as opposed to "low" dose rates of $\sim 10^{16}$ eV/gm-sec used by other workers⁽⁹⁾). On this basis, the dose rates in the

present experiment (in the range $[0.2-20] \times 10^{20}$ eV/gm-sec are low-to-intermediate. The present results, therefore, support the observations of Willis et. al.⁽⁶⁾, but not their interpretation.

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TABLE 1
Experimental Parameters

System Pressure p_s (Torr)	O ₂ Flowrate (std cm ³ /sec)	[O ₂] (10 ⁶ molecules per cm ³)	Irradiation Time, t_1 (sec)*	Elapsed Time to Sampling Point (sec)*	Proton Energy (Mev)	Proton Current Range† (μa)
1.72	5.46	0.849	0.293	0.347	0.90	1.0-2.1
2.12	6.74	1.18	0.260	0.310	0.90	0.2-0.5
2.50	7.95	1.50	0.240	0.287	0.90	0.1-0.3
2.92	9.30	1.84	0.229	0.275	0.90	0.1-0.5
3.45	11.0	2.35	0.211	0.255	0.94	0.1-0.7
3.92	12.5	2.82	0.200	0.243	0.91	0.1-0.9

* $t_1 = \int dx/v$, integrated over the appropriate section of the flow tube.

†Represents range covered by data at each pressure, not specific data points.

TABLE 2

Reaction of Gas Phase Radiolysis of Oxygen

A. Primary Reactions

B. Reactions of Neutral Species

<u>No.</u>	<u>Reaction</u>	<u>k, cm³/particle·sec</u>	<u>Reference</u>
(N-1)	$O + O_2 + O_2 \rightarrow O_3 + O_2$	$*6.5 \times 10^{-34}$	6
(N-2)	$O + O + O_2 \rightarrow O_2 + O_2$	$*2.7 \times 10^{-33}$	18
(N-3)	$O \rightarrow O_{ads}$	$**0.5$	19
(N-4)	$O_3 + O \rightarrow 2O_2$	9.3×10^{-15}	18
(N-5)	$O_3 + O_2 \rightarrow 2O_2 + O$	2.0×10^{-26}	18

C. Ion Reactions

(I-1)	$O^+ + O_2 \rightarrow O + O_2^+$	2.10^{-11}	6,20
(I-2)	$O_2^+ + O_2 \rightarrow O_4^+$	2×10^{-11}	6
(I-3)	$O^+ + e \rightarrow O$	3.3×10^{-8}	6
(I-4)	$O^+ + O_2^- \rightarrow O + O_2$	2×10^{-6}	6
(I-5)	$O^+ + O_4^- \rightarrow O + 2O_2$	2×10^{-6}	6
(I-6)	$O_2^+ + e \rightarrow 2O$	1.7×10^{-7}	6,20
(I-7)	$O_2^+ + O_2^- \rightarrow 2O + O_2$	2×10^{-6}	6
(I-8)	$O_2^+ + O_3^- \rightarrow O + 2O_2$	NA	
	$[O_2^+ + O_3^- \rightarrow 3O + O_2]$		
(I-9)	$O_2^+ + O_4^- \rightarrow 2O + 2O_2$	2×10^{-6}	6

TABLE 2 (Continued)

<u>No.</u>	<u>Reaction</u>	<u>k, cm³/particles·sec</u>	<u>Reference</u>
(I-10)	$O_4^+ + e \rightarrow 2O + O_2$	1.7×10^{-7}	6
(I-11)	$O_4^+ + O_2^- \rightarrow 2O_2 + 2O$	2×10^{-6}	8
(I-12)	$O_4^+ + O_3^- \rightarrow O_3 + 2O_2$	2×10^{-6}	6
(I-13)	$O_4^+ + O_4^- \rightarrow 2O + 3O_2$	2×10^{-6}	6
(I-14)	$O_2 + O + e \rightarrow O^- + O_2$	NA	
(I-15)	$O_2 + O_2 + e \rightarrow O_2^- + O_2$	$*1.4 \times 10^{-30}$	6, 20
	$[O_2 + e \rightarrow O_2^-]$	NA	
(I-16)	$O^- + O \rightarrow O_2 + e$	2×10^{-10}	20
(I-17)	$O^- + 2O_2 \rightarrow O_3^- + O_2$	$*4 \times 10^{-31}$	20
(I-18)	$O^- + O_3 \rightarrow O_3^- + O$	5×10^{-10}	20
(I-19)	$O_2 + O \rightarrow O_3 + e$	3×10^{-10}	20
(I-20)	$O_2^- + O_2 \rightarrow O_4^-$	7×10^{-11}	6
(I-21)	$O_2^- + O_3 \rightarrow O_3^- + O_2$	3×10^{-10}	6, 20
(I-22)	$O_3^- + O_3 \rightarrow O_2^- + 2O_2$	3×10^{-10}	21

*cm⁶/particle²·sec.

**sec⁻¹.

NA: not available

FIGURE CAPTIONS

1. Schematic of the Radiolysis Apparatus.
2. The Reaction Tube.
3. Measured Atomic Oxygen Concentration (atoms/cm³ at molecular beam source) as a function of total energy deposited (heV/cm³) for various flow conditions.
4. Measured ozone concentration (molecules/cm³ at molecular beam source) as a function of total energy deposited (heV/cm³) for various flow conditions.
5. Comparison of the measured dose-dependence of the atomic oxygen concentration with theoretical predictions for $p_s = 3.45$ Torr, $g_0 = 5$.
6. Comparison of the measured E_d - dependence of the ozone concentration with theoretical predictions for $p_s = 3.45$ Torr, $g_0 = 5$.
7. Measured atomic oxygen concentrations (top) and ozone concentrations (bottom) vs system pressure for $E_d = 2.5 \cdot 10^{12}$ heV-cm³. The curves are the calculated theoretical system response: A) simple model, $g_0 = 7.5$; B) full model, $g_0 = 24$; C) full model, $g_0 = 7.5$.
8. Comparison of modified simple model calculations with experimental results. $E_d = 2.5 \cdot 10^{12}$ heV/cm³; $g_0 = 1.1$; $g(0)_{eff} = 8.0$; $g_{O_2}^* = 12.5$; $k^* = 10$ (Torr-sec)⁻¹.

XBL 747-6777

Fig. 1

XBL 747 - 6774

Fig. 2

XBL747-6755
Fig. 3

XBL 747-6756
Fig. 4

XBL747-6758
Fig. 5

XBL 747-6759
Fig. 6

-34-

XBL 747-6757
Fig. 7

XBL 748-6954
Fig. 8

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