ANALYSIS OF REACTIONS ACTIVE DURING THE FORMATION OF OZONE IN A GAS DISCHARGE

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ABSTRACT

By using the known maximum ozone yield obtained in a gas discharge, it is shown, through a quantitative analysis, that only a certain number of reactions found have a sufficiently large cross-section to be of importance. From the obtained model, the influence of electric field and gas temperature on the ozone production is determined.

1. INTRODUCTION

The formation of ozone in a gas discharge is directly due to the recombination of an atom of oxygen with a molecule of oxygen, with the formation of atomic oxygen being due to the collisions between the electron swarm and the oxygen molecules. However, the number of reactions which can occur in oxygen leading to the above is very large [1] , there are, for example, thirty one reactions which can cause the formation of atomic oxygen, and twenty one which cause the formation of ozone. It can be readily supposed, however, that not all of these reactions will be of equal importance and the object of the present paper is to give a simple means of determining the principle reactions.

In the majority of previous studies [2] the onset energy for a particular reaction has been taken as being the main criterion for a discussion of it's relative importance, however, this is an over simplification of the problem since it is evident that it is the value of the mean cross-section for a particular value of the mean electron-energy encountered in the gas discharge which will determine the efficiency of a particular reaction. Mean cross-sections have already been calculated [3] from basic electron-beam data for the reactions important in the ionization growth in oxygen : Townsends first ionization coefficient α, etc. However, this has not been extended to the reactions which may be of importance in the formation of ozone (except for an early study[4] carried out before reasonably reliable cross-section and electron-energy data had been obtained). Also, up to the present time no simple means of relating the mean cross-section for a particular value of E/N (the electric field to gas density) to the electrical yield of ozone (which is the quantity measurable directly using a discharge device) has been given.

2. THEORY AND RESULTS

It will be initially assumed that each atom of oxygen formed by the gas discharge reacts to form ozone that is,

$$O + O_2 + O_2 \rightarrow O_3 + O_2 \qquad (1)$$

Now, the differential equation for the rate of ozone production can be written as,

$$\frac{d}{dt}[O] = \frac{d}{dt}[O_3] = \chi n_e v_e \qquad (2)$$

where O_3 is the number of ozone molecules, n_e is the number of electrons, v_e is the electron velocity, and χ is the number of oxygen atoms formed per electron per unit distance parallel to the electric field (χ/N is the mean cross-section). As all prebreakdown discharges (Trichel pulses, Townsend discharges, streamers, positive glow etc.) are composed of Townsend avalanches, only the ozone yield for one Townsend avalanche need be calculated.

The number of electrons in a Townsend avalanche under uniform field conditions after a time t from the start of the avalanche is,

$$n_e(t) = \exp(\alpha - \eta^*)\, v_e\, t \qquad (3)$$

where η^* is the virtual attachment coefficient. It should be noted that although this is a simplification [5] the value obtained is a very good approximation of the current in a Townsend avalanche [6].

By letting $\alpha - \eta^*$ equal $\bar{\alpha}$, substituting $n_e(t)$ in equation (2) and then integrating between $t = o$ and $t = \tau$ the number of ozone molecules formed in an avalanche is found to be,

$$[O_3] = \chi (\exp(\bar{\alpha} v_e \tau) - 1) / \bar{\alpha} \qquad (4)$$

and the corresponding mass of ozone formed is,

$$[O_3]g = M [O_3] / A_v \qquad (5)$$

where A_v is Avagadro's number and M is the gram molecular weight of ozone.

In order to calculate the maximum electrical yield only the energy(E_n) dissipated by the electrons formed in the avalanche will be considered, thus,

$$E_n = V \int_0^\tau I_e(t)\, dt \qquad (6)$$

where V is the voltage across the avalanche distance d ($d = v_e \tau$). The electron current at a time t is,

$$I_e(t) = I_e(0) \exp(\bar{\alpha} v_e t) \qquad (7)$$

where $I_e(0)$, the initial electron current, is equal to q/τ (q is the electron charge). Substituting $I_e(t)$ in equation (6) and then integrating gives the energy dissipated

$$E_n = q (\exp(\alpha v_e \tau - 1) / \bar{\alpha} d \qquad (8)$$

The electrical yield can now be obtained from equations (5) and (8);

$$[O_3]\, g / E_n = M \chi d / q A_v V \ \text{g/joule} \qquad (9)$$

By letting d take any value it can be assumed, even for a nonuniform field, that the electric field E is equal to V/d, and by substituting values for M, A_v and q, and changing the units to g/kwh, gives,

$$[O_3]\ g\ /\ E_n = 1500\ (\ \chi\ /\ N\ )\ /\ (\ E\ /\ N\ )\ g/kwh \qquad (10)$$

The rate of ozone formation can be obtained directly from equation (9) and is,

$$\frac{d}{dt}[O] = \left(\frac{Vj}{qd}\right)\left(\frac{\chi/N}{E/N}\right)\ atoms\ /\ cm^3\ -\ sec. \qquad (11)$$

where j is the current density.

(It should be noted that although the present study is restricted to ozone formation, the above equation (10) can be used to determine the maximum electrical yield for any reaction which is dependant on an electron collision process in any gas if the mean cross-section for the reaction is known). The maximum ozone yield obtained experimentally is of the order of 400 g/kwh[7,8,9] which is in agreement with that postulated by Lunt [10] and thus this value will be used in the present analysis. In the above experimental cases, the value of E/N was of the order of 10^{-15} V cm^2 and it follows from equation (10) that, for the required yield the mean cross-section must be of the order of 10^{-16} cm^2 . Now, the total cross-section in oxygen is $\sim 10^{-15}$ cm^2 and thus a reaction with a relativery large cross-section, $\sim$ 1/10 of the total, is required to explain the experimentally obtained ozone yields.

From the known cross-section data[11,12] it appears that the only reactions which have a sufficiently large cross-section to account for the formation of atomic oxygen are the following dissociative reactions,

$$e + O_2 \rightarrow O_2[A^3\ \Sigma_u^+] + e \rightarrow O\ (^3P) + O\ (^3P) + e \qquad (12)$$

$$e + O_2 \rightarrow O_2[B^3\ \Sigma_u^-] + e \rightarrow O\ (^3P) + O\ (^1D) + e \qquad (13)$$

(These reactions have onset energies of $\sim$ 4.5 eV and 8 eV and maximum cross-sections of $\sim 2.10^{-17}$ cm^2 and $\sim 8.10^{-17}$ cm^2 respectively). In order to test whether only the dissociation of oxygen need be considered to explain the formation of ozone, the ozone yield as a function of E/N was determined and compared with experimentally-obtained results. The mean cross-section for dissociation was found by folding the dissociation cross-section distribution into the electron-energy distribution. This was carried out by assuming a Maxwell-Boltzman distribution for the electrons, by using the mean electron-energy data as given by[13] , and by taking the cross-section to be $2.10^{-17} cm^2$ for electron energies between 4.5 and 8 eV and 10^{-16} cm^2 for energies greater than 8 eV (the absence of a higher voltage above which the cross-section becomes negligibly small is of no significance as the number of correspondingly energetic electrons is negligible under the discharge conditions considered). The ozone yield was then directly obtained by application of equation (10). There is close agreement between the calculated results and those obtained by Warburg and Rump [14] .We can therefore draw the conclusion that the dissociation of oxygen is the principle reaction in the formation of ozone. However, their results[14] were obtained at a relatively low neutral gas temperature (the current density being kept feeble,$\sim$ 8 $\mu A/cm^2$), while those of Brewer and Westhaver [15] , which give a much lower ozone yield (although with the same characteristic variation) were obtained

at a higher temperature (the current density being $\sim$ 1 mA/cm^2). It therefore follows that the initial assumption, whereby each oxygen atom forms one ozone molecule, is only valid at low temperatures / current densities and that at higher neutral gas temperatures other reactions (which are a function of this temperature and not the electron temperature) must be taken into consideration : these reactions will therefore be due to atom/molecule etc. type collisions between the three molecules of importance O, O_2 and O_3 such that the atoms of oxygen or the molecules of ozone are lost. Again, there are a large number of possible reactions [1] with fifteen known for the distruction of ozone and twenty five for the distruction of atomic oxygen. However, by considering the known reaction rates [16] it would appear that only the following are of importance,

$$O_3 + O_2 \rightarrow O_2 + O_2 + O \qquad (14)$$

$$O + O_3 \rightarrow 2\,O_2 \qquad (15)$$

$$O + O + O_2 \rightarrow 2\,O_2 \qquad (16)$$

By taking the above reactions, the differential equations describing the formation of ozone in a gas discharge can therefore be written as,

$$\frac{d}{dt}[O] = (2\,Vj/qd)\,(\chi/P)/(E/P) - k_1[O][O_2]^2 + k_2[O_3][O_2] - k_3[O][O_3] - k_4[O]^2[O_2] \qquad (17)$$

$$\frac{d}{dt}[O_2] = -(2Vj/qd)\,(\chi/P)/(E/P) - K_1[O][O_2]^2 + k_2[O_3][O_2] + k_3[O][O_3] + k_4[O]^2[O_2] \qquad (18)$$

$$\frac{d}{dt}[O_3] = k_1[O][O_2]^2 - k_2[O_3][O_2] - k_3[O][O_3] \qquad (19)$$

These equations can be solved using a numerical integration technique, such as that of Runge-Kutta, for the variation in the concentration of ozone with time and temperature in any discharge.

In order to test whether this model did indeed describe the formation of ozone in a gas discharge a computer run was carried out [17] using the same discharge parameters as given by [7]. Figure 2 shows the variation in the saturated ozone concentration with temperature (given in degrees Kelvin) and it can be seen that the experimentally determined values [7] decrease more with temperature than indicated by calculation. This can be explained as follows : In order to determine the temperature Devins [7] measured the average value over the whole discharge region. This is unlikely to give the mean temperature since the discharge current was pulsating and thus, if, as is suggested here, the mean temperature during the discharge is $\sim$ 1.14 the average value, then a satisfactory fit can be obtained between the experimental and calculated results for the variation in the ozone concentration with temperature.

CONCLUSIONS

1. A means of determining the electrical yield for electron/molecule type reactions is given.
2. For the formation of ozone, it is shown that oxygen dissociation is the principle reaction.
3. At low neutral gas temperatures (less than $\sim$ 25°C) it can be assumed

that all oxygen atoms created in the discharge react to form ozone. At higher temperatures the reactions (14 - 16) must be taken into consideration.

4. If the basic parameters (E/N, j, T) are known then the present model can be used to predict the ozone yield in any gas discharge device.

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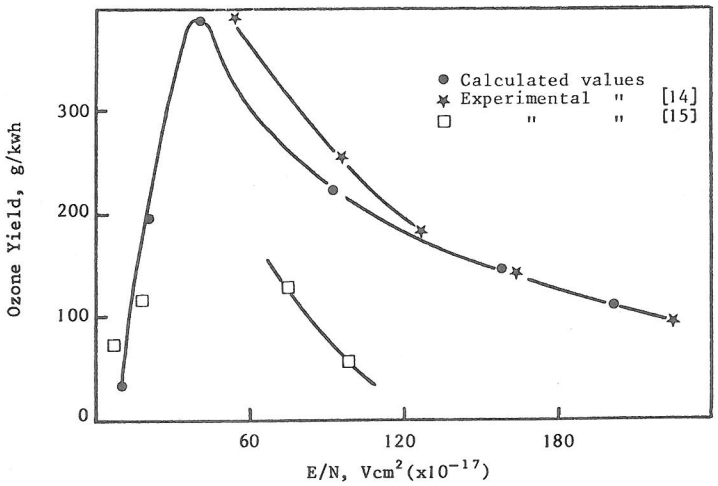

Fig. 1. Variation in Ozone yield with E/N

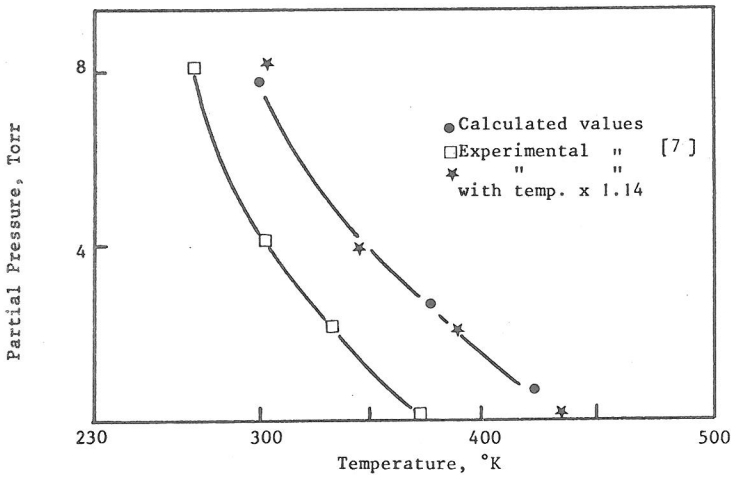

Fig. 2. Variation in Ozone concentration with temperature