ON THE PLASMA CHEMISTRY OF ATOMIC OXYGEN WITHIN AND DOWNSTREAM FROM A DC DISCHARGE IN FLOWING O_2

H. Sabadil
Sektion Physik/Elektronik, E.-M.-Arndt-Universität
Greifswald, 22 Greifswald, DDR

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ABSTRACT

The ozone method has been used successfully to provide data for the concentration of atomic oxygen at the exit of the discharge and for its spatial variation in the flowing afterglow. The attention is paid to the influence of pressure (0,60 - 4,0 torr) and current (2 - 100 mA) on the plateau of the O curves observed in the early afterglow. These results show that the main channel for O production is the interaction of O_3 with energetic species (probably: $O_2(^1\Delta_g, v = 1)$).

1. INTRODUCTION

The dissociation of molecular oxygen in electrical discharges has been a subject of numerous investigations (1-12). For low pressure conditions dissociation by direct electron impact has been considered as the prevailing mechanism of the production of O atoms (2-8). With increasing pressures vibrationally excited molecules were assumed to play an important role for the dissociation (9). This paper reports the results of an experimental study of variation of [O] in the flowing afterglow, which give important insights into production processes of O atoms within low pressure discharges.

2. EXPERIMENTAL

The ozone method of measuring the O concentration used in these studies have been described in detail in (6,10,11) and will be discussed briefly here. The base of this method is the heterogeneous reaction, $O + O_2 \cdot S \longrightarrow O_3 \cdot S$, taking place on a surface S cooled with liquid nitrogen. The surface S is realized by the internal wall of an U shaped flow tube (see fig.1). For each of the O atoms, which reaches the cold wall, one O_3 molecule is formed. The procedure of [O] measuring is as follows: During the running time t_B of the discharge the U tube is surrounded by liquid nitrogen. The ozone is deposited as a blue liquid film ring at the cold wall of that part of the U tube which is connected with the discharge tube. After the current cut-off and the interruption of the gasflow the tube system is evacuated to about 10^{-3} torr. Then the liquid nitrogen is removed and a discharge in O_3 causes a conversion to O_2. Finally, the pressure $p_{O2} = (3/2) \cdot p_{O3}$ can be measured. Under fast flow conditions the axial diffusion of O may be neglected and the parameter p_{O3}/t_B and the degree of dissociation

$$\beta = \frac{[O]}{2[O_2]+[O]}$$

are related by the equation

$$\beta = \frac{\left(\frac{p_{O3}}{t_B}\right) V}{2F}$$

V is the volume of the discharge tube and the U tube; F means the flow rate of molecular oxygen fed to the discharge. The pressure p in the tube system is used together with F measured in $\text{torr} \cdot l \cdot s^{-1}$-units and the cross-sectional area πr^2 of the U tube, to give the bulk velocity of the gas v_u :

$$v_u = \frac{F}{\pi r_u^2 p}$$

The residence time of the atomic oxygen in the flow tube volume between the exit of the discharge and the position of the surface of liquid nitrogen is then: $$t_u = \frac{\ell}{v_u}$$

3. RESULTS AND DISCUSSION

In contrast to our studies in (6) the measurements of O were performed at enlarged velocities v_u, so that the variation of [O] can be followed for small times t_u outside the discharge region. This paper reports measurements of [O] in the flow tube U3. It is mentioned here that under the same discharge conditions the values of [O] at the exit of the discharge are smaller in the tubes U1 and U5 than the corresponding value of [O] in the tube U3 due to additional O loss in the electrode regions. Details relating to this observation will be published elsewhere. Plots of in the flow tube U3 as a function of t_u are shown in fig.2 for a series of currents. One feature is apparent, and that is a total absence of any O atom decay at small residence times. These experiments suggest the presence of energetic species capable of producing O atoms in a region without electrons, so that the O loss in the volume and on the wall is compensated. Furthermore we see from figures 2 and 3 that the width of the plateaus decreases with increasing current and pressure. We found a similar dependence of the width of plateaus on current and pressure also for the curves in the flowing afterglow of a discharge tube with 5,4 int. diameter. It must be noted that previously Kaufmann and Kelso (1) observed the same behaviour of [O] downstream a microwave discharge. In this paper it was measured the intensity of $O + NO \rightarrow NO_2 + h\nu$ light emission by means of a photomultiplier movable along the flow tube. For more detailed understanding of the plateau calculations of $[O]$ as function of t_u were carried out considering the following reactions:

(I) $O + \text{wall} \longrightarrow \frac{1}{2} O_2$, $k_1 = \frac{\gamma \omega}{2 r_u} = 10\, s^{-1}$

(II) $O + 2O_2 \longrightarrow O_3 + O_2$, $k_2 = 6{,}0 \cdot 10^{-34}\, cm^6 s^{-1}$

(III) $O + O_3 \longrightarrow 2O_2$, $k_3 = 6{,}2 \cdot 10^{-15}\, cm^3 s^{-1}$

(IV) $O_2(^1\Delta_g) + O_3 \longrightarrow 2O_2 + O$, $k_4 = 3{,}5 \cdot 10^{-15}\, cm^3 s^{-1}$

(V) $O_2^* + O_3 \longrightarrow 2O_2 + O$, (VI) $O_2^* + (\text{wall or } O_2) \longrightarrow O_2$

In (12) the observation $[O]$= const for small t_u has been explained with the help of reaction (IV). But it follows from our calculations that the rate coefficient of (IV) is much too small in order to explain the plateau (10,11). Therefore it is necessary to assume additional energetic species O_2^* to be present in O_2 emerging from the discharge which produce O atoms corresponding (V). From energetic point of view $O_2(^1\Delta_g, v=1)$ should be effectively in dissociation of O_3 (13). But unequivocal positive identification of O_2 must await further study. Therefore the values of k_5 and k_6 must be assumed arbitrately: $k_5 = 8{,}0 \cdot 10^{-13}\, cm^3 s^{-1}$, $k_6 = 27\, s^{-1}$
The system of the rate equations taking into account the processes (I)-(VI) have been solved with a computer. The dashed curve in fig.2 demonstrates the calculated β as function of t_u for following values at the exit of the discharge:

$[O] = [O_2(^1\Delta_g)] = 6{,}0 \cdot 10^{15}\, cm^{-3}$, $[O_3] = 8{,}0 \cdot 10^{13}\, cm^{-3}$
$[O_2^*] = 1{,}0 \cdot 10^{16}\, cm^{-3}$; $p = 1{,}0$ torr

If the ratio $[O]/[O_2^*]$ decreases the calculations provide a more extensived plateau. Thus, the inclusion of reaction(V) provides an explanation for β =const for small t_u. It must be emphasized that under low pressure conditions the production of O_3 proceeds dominately via $O^- + O_2(^1\Delta_g) \rightarrow O_3 + e$ inside the discharge. Because the transition from the discharge to the early afterglow region takes place continuously the observations of the plateau are meaningful in the sense that they indicate a O production process within the discharge with a rate which exceeds that of dissociation by direct electron impact. This statement has been confirmed by calculations of impact rates of the last process using the dates in (7,8) and that of reaction V. If the mechanism (V) is operative, the variation of the plateau width with the current in fig.2 strangly suggest a decrease of $[O_3]$ with increasing current. Therefore absorption measurements (at λ=2537 Å) were carried out to determine the relationship between $[O_3]$ and the current. Some of the results of these experiments are shown in fig.4. In fact, it will be seen that $[O_3]$ reaches a maximum at current of about 15 mA and then decreases significantly with increasing current.

REFERENCES

(1) F. Kaufman and J. R. Kelso, Disc.Farad.Soc.37,26(1964).

(2) P.D. Francis, Brit.J.Appl.Phys.2,1717(1969).

(3) A.M. Mearus and A. Morris, J.Chem.Eng.Progr.Symp. Ser.67,37(1971).

(4) A.T. Bell and K. Kwong, AichE J. 18,990(1972); Ind.Eng.Chem.Fundam. 12,90(1973).

(5) P. Kocian, J.M. Marior, XIII ICPIG,I,253,Berlin(1977).

(6) H. Sabadil, L. Biborosch and G. Koebe, Beitr.Plasma-Phys.15,319(1975).

(7) K. Masek, L. Laska, T. Ruzicka, Czech.J.Phys.B.28,1321

(8) L. Laska, K. Masek, T. Ruzicka, Czech.J.Phys.B.29, (1979).

(9) P. Capezzuto, F. Cramarossa, R. D'Agostino and E. Molinari, J.Phys.Chem.79,1487(1975) J.Phys.Chem.80,882(1976).

(10) H. Sabadil and E. Zielke, XIII ICPIG,I,249,Berlin(1977)

(11) H. Sabadil, Sektion Physik/Elektronik,Greifswald, Report 1977/78.

(12) M. Yaron and A. von Engel, III Int.Symp. on Plasma Chemistry G2,24 Limoges (1977).

(13) F. Gresteau, R.I. Hall, J. Mazeau and D. Vichon, J.Phys.B:10,L545(1977).

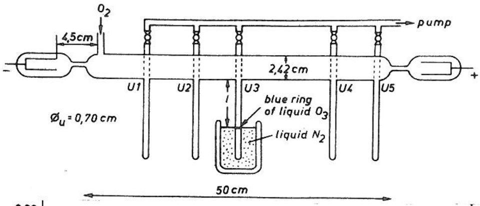

Fig.1

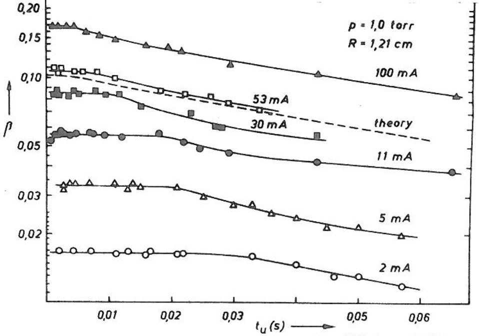

Fig.2

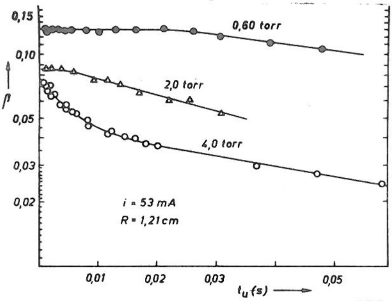

Fig.3

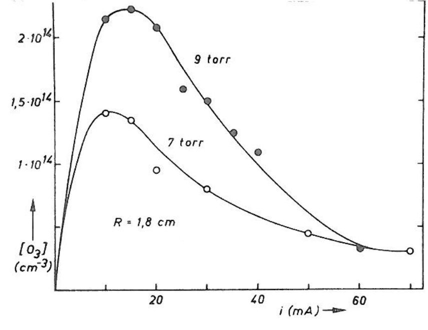

Fig.4