# Pressure Dependence of the Yield of Ozone from the Pulse Radiolysis of Oxygen at High Dose Rates

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*Summary* The yield of $O_3$ (molecules/100 ev) from a high dose-rate radiation pulse in $O_2$, decreases with increasing $O_2$ pressure and it is postulated that this is due to a competition between electron capture by $O_2$ and ion–electron recombination.

THE ozone formed when oxygen is irradiated with an electron pulse can readily be measured by its absorption in the u.v.[1] and this system has been recommended as a convenient dosimeter for gas-phase pulse radiolysis.[2] An absolute value, $G(O_3) = 13{\cdot}8 \pm 0{\cdot}7$ molecules per 100 ev, from $O_2$ at 1 atm., was determined[2] using a 30 nsec. pulse of electrons from a field-emission source. Using a pulse of similar dose-rate, (*i.e.* approximately $5 \times 10^4$ ev molecule$^{-1}$ sec.$^{-1}$), we find that $G(O_3)$ is dependent on the $O_2$ pressure in the range 200—2000 torr. This is of significance in the interpretation of the mechanism of $O_2$ formation and should be taken into account when this system is used as a dosimeter.

Oxygen was pulse irradiated with electrons (maximum energy approximately 500 kev) from a Febetron Model 706 (Field Emission Corporation) the half peak-height duration being about 3 nsec. As in previous work[1,2] the formation of $O_3$ was followed by kinetic spectroscopy, the absorption at 256 nm being measured with a photomultiplier and oscilloscope arrangement, and the growth of the absorption corresponded to first order formation of $O_3$. The increase in absorption due to a single pulse was measured after a steady value had been reached (typically 100 $\mu$sec. after the pulse). In pure $O_2$ the optical density change per torr ($Y_{O_3}$) is dependent on $O_2$ pressure ($P_{O_2}$) but with $SF_6$ present (1 mole%) no dependence on $P_{O_2}$ is observed (Figure).

Assuming the absorbed dose per pulse to be proportional to $P_{O_2}$, it is possible that the dependence of $Y_{O_3}$ on $P_{O_2}$ is due to a competition between ion–electron recombination and electron capture by $O_2$. Recombination of the positive ion ($O_4^+$ at the pressures used[3]) with electrons would be expected to give $O_3$ *via* reaction (1)

$$O_4^+ + e^- \rightarrow 2O + O_2 \qquad (1)$$

(each oxygen atom reacts to give $O_3$).[1] When electron capture by the net three-body reaction (2)

$$e^- + O_2 + O_2 \rightarrow O_2^- + O_2 \qquad (2)$$

occurs, neutralization will involve ion–ion recombination and if it does not result in $O_2$ dissociation[4] the $O_3$ yield will be lowered. With $SF_6$ present at a sufficiently high concentration, $e^-$ capture by $SF_6$ to give $SF_6^-$ occurs to the exclusion of reaction (1) with a consequent depression of the $O_3$ yield, assuming that neutralization of $O_4^+$ by $SF_6^-$ does not give $O_3$. In pure $O_2$, therefore, as $P_{O_2}$ is increased, competition of reaction (2) with reaction (1) should depress $Y_{O_3}$ towards a limiting value, equal to that obtained with $SF_6$ present. Assuming stationary state conditions during the pulse, the competition between reactions (1) and (2) gives $\Delta Y_{O_3}^{-1} = (Y_{O_3})_e^{-1}(1 + k_1^{-1}k_2[O_2]^2[O_4^+]_S^{-1})$ where $\Delta Y_{O_3}$ is the difference between the values of $Y_{O_3}$ in the absence and presence of $SF_6$, $(Y_{O_3})_e$ is the maximum yield of $O_3$ from reaction (1), *i.e.* when all of the electrons undergo this reaction, and $[O_4^+]_S$ is the stationary concentration of ions. Since $[O_4^+]_S$ may be assumed to be proportional to (dose rate per unit volume)$^{0{\cdot}5}$ and, therefore, proportional to $P_{O_2}^{0{\cdot}5}$, a linear dependence of $\Delta Y_{O_3}^{-1}$ on $P_{O_2}^{1{\cdot}5}$ would be expected from this mechanism. This conclusion is consistent with the results: the upper line in the Figure has been calculated from a linear plot of $\Delta Y_{O_3}^{-1}$ against $P_{O_2}^{1{\cdot}5}$.

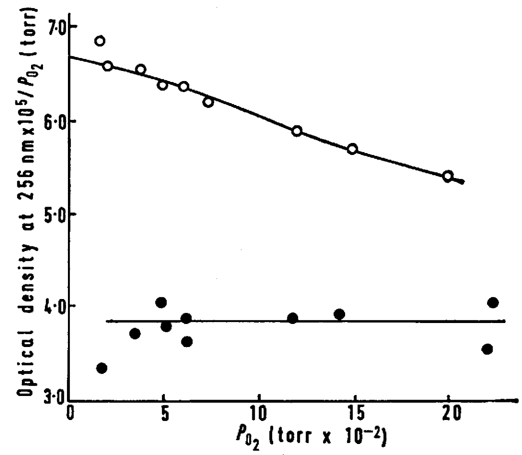


FIGURE. $O_3$ *Formation in the pulse radiolysis of* $O_2$ *at high dose rates: dependence of* $O_3$ *yield (pulse*$^{-1}$ *torr*$^{-1}$*) on* $O_2$ *pressure: open circles, pure* $O_2$*; line calculated as described in text: filled circles,* $O_2 + SF_6$ *(1 mole%).*

The absolute $O_3$ yield ($G = 13{\cdot}8 \pm 0{\cdot}7$) reported[2] for pulse radiolysis of $O_2$ is greater than that for $\gamma$-radiolysis ($G = 10{\cdot}6$)[4,5] and it has been suggested[6] that this may be due to a change in the neutralization process in going from high to low dose rates. We have not measured the absolute yield but the contribution of reaction (1) to $O_3$ formation may be deduced if it is assumed that the total limiting yield at low $P_{O_2}$ (Figure) is $G = 13{\cdot}8$ (ref. 2). On this basis the yield of $O_3$ from reaction (1), given by the maximum depression by $SF_6$, $(Y_{O_3})_e$, is $G = 5{\cdot}9$. This is reasonably close to the value expected ($6{\cdot}5$) if reaction (1) is the only ion recombination process and gives two molecules of $O_3$ per electron [$W(O_2) = 30{\cdot}6$ ev/ion pair[7]]. The residual yield ($G = 7{\cdot}9$) in the presence of $SF_6$, which is due to processes other than ion neutralization, is less than the $\gamma$-ray value. This suggests that while the contribution to $G(O_3)$ from ion–electron recombination increases in going from low to high dose rates the contribution from other processes decreases.

It has recently been found[8] that anomalous yields are

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obtained when certain gases (*e.g.* HCl, HBr, $N_2O$) are pulsed at high dose rates with Febetron machines, the *G*-values for product formation increasing with decreasing pressure below about 700 torr. This effect is ascribed[8] to the acceleration of secondary electrons in transient electrical fields created by the pulse. In confirmation of this finding, we have obtained[9] similar results with $C_3H_8$, $C_2H_4$, and $N_2O$. However, anomalous pressure effects of this type do not appear to play a significant part in the experiments with $O_2$ reported here. This is apparent from a comparison of the form of the pressure dependence in the Figure with that observed in the other systems mentioned above and, also, from the fact that $Y_{O_3}$ is independent of $P_{O_2}$ when $SF_6$ is present. Furthermore, we have also investigated[9] the sensitized formation of $O_3$ in $Ar-O_2$ and $CO_2-O_2$ mixtures, where the $O_3$ yield per pulse is proportional to $P_{Ar}$ and $P_{CO_2}$, and find no evidence of anomalous pressure effects in these systems.

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