ENHANCEMENT OF OZONE EFFICIENCY IN THE REACTIONS OF O₂ AND ACTIVATED N₂ MOLECULES IN AN AIR OZONIZER

S. Okazaki, H. Okamura, M. Miyamoto, M. Kogoma and T. Moriwaki
SOPHIA UNIVERSITY, FACULTY OF SCIENCE & TECHNOLOGY, 7-1 KIOCHO CHIYODA-KU TOKYO 102, JAPAN

Abstract
The energy efficiency of ozone formation in a Welsbach type ozonizer rose to 25% by the addition of 0.08% SF₆ in air. The main reactions which cause the ozone efficiency to rise are reactions via activated N₂ molecules above 90%. The dissociation of activated N₂ molecules on the surface is the rate-controlling step for NOₓ formation.

1. Introduction
The mechanism of ozone generation in the silent electric discharge of an oxygen ozonizer has been studied by several investigators (1) (3). Ozone is usually formed by O atoms and activated O₂ through reactions (1) to (3);

\[ \text{O}_2 \rightarrow \text{O}_2^* \rightarrow 2 \text{O} \] (1)

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \] (2)

\[ \text{O}_2^* + \text{O}_2 \rightarrow \text{O}_3 + \text{O} \] (3)

The mechanism of NOₓ formation in air ozonizers which are usually used has been studied by few investigators (4), (5), (6). We have confirmed (6) the existence of the mechanisms of ozone generation via activated N₂ molecules and N atoms from the fact that ozone efficiency in an air ozonizer rose to 30% by the addition of SF₆. In this paper we give a detailed analysis of this mechanism of ozone generation in an ozonizer of N₂/O₂ mixtures.

2. Experimental
We used an industrial Welsbach type ozonizer in this study. The glass tube has a diameter of 7.4cm and a length of 70cm. The outside electrode is made of stainless steel. The gap separation is 1.2mm and the electrode area is 350cm². The stainless steel electrode and glass tube were cooled by a liquid of low electrical conductivity (silicon oil and methanol). N₂ and O₂ gases were mixed with 0-0.2% SF₆. Water was removed from the gas mixture by a CH₃CN-dryice trap at -50°C; then the mixture was cooled to 0°C. Gas mixtures were
supplied with an ozonizer under the experimental conditions in Table 1.

The concentrations of \( \text{O}_3 \) and \( \text{NO}_x \) were measured using the UV absorption of 254nm, the KI titration method and a chemiluminescence NO\(_x\) meter. The power consumption in an ozonizer of the silent electric discharge, and the sustaining voltage in the discharge were both determined\(^3\) from the Voltage-Current Lissajous' figures displayed on the screen of a oscilloscope.

3. Results and Discussion.

1) The effect with SF\(_6\) in each \( \text{O}_2 \) mole fraction.

The ozone efficiencies in oxygen and air were reported to be 220g(kWh\(^{-1}\)) and 90g(kWh\(^{-1}\)), respectively, in a small ozonizer in a previous report.\(^6\) Although they are lower in this report, where a large ozonizer was used, for example 190g(kWh\(^{-1}\)) in oxygen and 85g(kWh\(^{-1}\)) in air, this is no problem. We will discuss the increase in ozone efficiency when SF\(_6\) is added.

Fig. 1 shows ozone efficiencies in each \( \text{O}_2 \) mole fraction without SF\(_6\) (b) and with SF\(_6\) (c). If an electronic energy partition between the \( \text{O}_2 \) and \( \text{N}_2 \) molecules is practically proportional to the mole fractions\(^8\) and if ozone is only formed by Reactions (1) to (3), ozone efficiency will follow the dashed line (a) in Fig. 1. But (b) is above (a); particularly in air, the increase in ozone efficiency is more than two times (a). These facts, along with the \( \text{N}_2 \) catalytic activation by adding SF\(_6\)\(^10\) and the increase\(^6\) in ozone efficiency when SF\(_6\) is added in an air ozonizer at point X in Fig. 1, allowed us to report that ozone was formed by the reaction via activated \( \text{N}_2 \) molecules and N atoms with Reactions (1) to (3).

In this experiment, curve (c) in Fig. 1 shows maximum ozone efficiency in each \( \text{O}_2 \) mole fraction when SF\(_6\) is added. Table 2 shows the best conditions with SF\(_6\) in each \( \text{O}_2 \) mole fraction. Fig. 1 (c) shows that there is no effect with SF\(_6\) in pure \( \text{O}_2 \); this effect with SF\(_6\) occurs only in \( \text{N}_2/\text{O}_2 \) mixtures. We again confirmed over a wide concentration range that ozone is formed by the reaction of an activated \( \text{N}_2 \) molecule and a \( \text{N} \) atom.

The addition of SF\(_6\) in an ozonizer will be useful, particularly in air which is more often used industrially. The ozone efficiency in an air ozonizer rose to 25% when SF\(_6\) was added. The NO\(_x\) concentration was about 2.4% of the \( \text{O}_3 \) concentration when SF\(_6\) is added(Table 2). This poses no problem for industrial use.

2) The mechanism of ozone generation via activated \( \text{N}_2\).

The mechanism of ozone generation may be Reactions (4) to (13) via activated \( \text{N}_2 \) molecules and N atoms, in addition to the former Reactions (1) to (3) via activated \( \text{O}_2 \) molecules. These new reactions are shown in Table 3.

In general, the direct electronic-exitation states from the ground state \( \text{N}_2 (X^3\Sigma_g^-) \) are directly \( \text{C}^3\Pi_g \) in Frank-Condon theory over this \( E7N \) range and a metastable state \( \text{N}_2 (A^3\Sigma_u^+) \)
is formed, following by the radiative and collisional cascade process shown in Table 4. The radiative time and potential energy of activated \( N_2 \) molecules \( N_2(C^3Pi_g), (B^3Sigma_u^+), \text{or} (A^3Sigma_u^+) \), are shown in Table 4. \( N_2(A^3Sigma_u^+) \) has a long radiative life time (Vegard-Kaplan emission, \( t \approx 2s \)), but is highly reactive. The average time between collisions in the atmosphere is about \( 10^{-8} - 10^{-9} \) sec. and the dissociative energy of the \( O_2 \) molecule is about 5.1 eV. We thought that most of activated \( N_2 \) molecules in the atmosphere reacting with \( O_2 \) molecules via almost \( N_2(A^3Sigma_u^+) \).

If we consider Reactions (6) to (11) of \( N_2(A^3Sigma_u^+) \) with \( O_2 \) molecules, we find that \( N_2(A^3Sigma_u^+) \) may be destroyed by collisions with ground state \( N_2 \) molecules, such as Reaction (14) in \( N_2/O_2 \) mixtures. The rate constants for Reactions (14) and (6) to (11) reported by Levron [11] and Kaufman [12] show that equation (15) is allowed under this experimental condition, the possibility that \( N_2(A^3Sigma_u^+) \) is destroyed by collisions with \( N_2 \) molecules can be neglected.

3) The branching ratio of Reactions (4) to (12).

We estimated the branching ratio of energetic Reactions (6) to (12) by measuring ozone formation and \( NO_x \) formation when \( SF_6 \) was added. The conditions for the estimate are as follows;

Reaction (9) is negligible because \( O(1^D) \) formation was not observed in the reaction of \( N_2(A^3Sigma_u^+) \) with \( O_2 \) molecule at low pressure. [13] Reactions (10) and (11) are reactive channels: (10) is a four-center reaction to form two \( NO \), and (11) requires an unlikely rearrangement in which two bonds are broken and two other formed. There is no experimental evidence for either (10) or (11), so we neglect them. [13], [14]

Finally we considered Reactions (6), (7), (8) and (12) for ozone formation. [13]

Two ozone molecules are formed by Reactions (6) and (7) and one ozone molecule is formed by Reactions (8) and (12). Similarly one \( NO_x \) molecule is formed by Reaction (12).

The branching ratio of Reactions (6), (7), and (8) are 65, 33, 2 by Kaufman. [13]

We estimated the branching ratio which makes the theoretical increase in the \( (NO_x/O_3) \) ratio agree with the experimental increase in \( (NO_x/O_3) \) ratio, from (a) to (b) and (b) to (c) in Fig.1. Some examples are shown in Table 5 for each \( O_2 \) mole fraction. They show that ozone is formed by Reactions (6) and (7) via an activated \( N_2 \) molecule above 90% when \( SF_6 \) is added.

We also carried out experiments which increase the surface area in an ozonizer by inserting glass wool, to confirm that channels exist for \( NO_x \) formation. As a result of Reaction (13), \( NO_x \) formation and the branching ratio of Reaction (12) via \( \text{N} \) atoms are practically increased (Table 5). So a channel exists for \( NO_x \) formation, passing through Reaction (13) via (12).

4) Ozone and \( NO_x \) formation

We tried to estimate whether \( NO_x \) formation is initiated
by Reaction (4) or by Reaction (5). Ozone is clearly formed by volume reactions (1) to (3) via (4) via (6) and (7). The ozone current efficiency rose sharply when the gap separation changed from 1mm to 3mm(Fig.3 -O-, -O-, -Δ-). Changing the gap separation from 1mm to 3mm means that the trajectory of an electron is longer. It is clear that NH₃ is only formed on surfaces. [5, 16] Indeed the NH₃ current efficiency is constant from 1mm to 3mm(Fig.2). On the other hand, the NOₓ current efficiency rose slightly(Fig.3 -O-, -O-, -Δ-). Therefore, volume reaction (5) via (12) exists for NOₓ formation. However, NOₓ and NH₃ formation are of the same order(10⁻⁶ mol s⁻¹) and are one-hundredth that of ozone formation. As a result of inserting glass wool, the NOₓ current efficiency rose sharply, but the ozone current efficiency did not change because ozone is formed by volume reactions(Fig. 3 -O-, -O-). Therefore, most NOₓ is formed by Reaction (4) via (13) via (12), which activated N₂ molecules are dissociated on surfaces. Fig. 4 shows the change of rising ratio in ozone and NOₓ current efficiency when SF₆ is added. There is a similar relationship in each O₂ mole fraction. So we can consider that ozone formation and NOₓ formation when SF₆ is added will be initiated by the same mechanism: Reaction (4).

4. Conclusion

SF₆ catalytically increased activated N₂ molecules. The initiative reaction in both ozone and NOₓ formation is N₂(A²Σ u⁺) formation(4). Ozone is formed by volume Reaction (4) via (6) and (7) above 90% when SF₆ is added. The dissociation of activated N₂ molecules on the surface is the rate-controlling step for NOₓ formation.

Acknowledgement

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References

2) S.W. Benson, Ozone Chem. and Tech., Adv. in Chem. Ser., 21, 398(1959)
Table 1. Experimental conditions

| Flow rate | 33.3 cm$^3$ s$^{-1}$ |
| Frequency | 50 Hz               |
| Pressure  | 1 atm               |
| Applied voltage | 5-10 kV |

Table 2. The best conditions of ozone formation

<table>
<thead>
<tr>
<th>$[O_2]/([O_2]+[N_2])$</th>
<th>SF$_6$/%</th>
<th>V/kV</th>
<th>R/%</th>
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<td>5.5</td>
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</tr>
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<td>0.025</td>
<td>6.0</td>
<td>4.6</td>
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<tr>
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<td>0.01</td>
<td>5.5</td>
<td>4.8</td>
</tr>
<tr>
<td>1.0</td>
<td>added</td>
<td>5-10</td>
<td>0</td>
</tr>
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</table>

$[N_2]/[O_3]$ | 1.9% (Air alone) | 2.4% (with 0.08% SF$_6$)

The mechanism of ozone generation

$$O_2 \rightarrow O_2^* \rightarrow 20 \ (1)$$

$$O + O_2 + M \rightarrow O_3 + M \ (2)$$

$$O_2^* + O_2 \rightarrow O_3 + O \ (3)$$

$$N_2 + e \rightarrow N_2(A^3\Sigma_g^+) + e \ (4)$$

$$\rightarrow 2N(2^3D, 4^3S) + e \ (5)$$

$$N_2(A^3\Sigma_g^+) \rightarrow O_2 \ (6)$$

$$\rightarrow N_2(X^1\Sigma_g^+) \rightarrow 20(3^3P)$$

$$\rightarrow N_2(X^1\Sigma_g^+) \rightarrow O_2^* \ (7)$$

$$\rightarrow N_2O \rightarrow O(3^3P) \ (8)$$

$$\rightarrow N_2O \rightarrow O(1^3D) \ (9)$$

$$\rightarrow 2NO(X^2\Pi) \ (10)$$

$$\rightarrow NO^+ \rightarrow N^+(S) \ (11)$$

$$N(2^3D) + O_2 \rightarrow NO + O(3^3P) \ (12)$$

$$N_2(A^3\Sigma_g^+) \rightarrow 2N(2^3D, 4^3S) \ (13)$$

Table 4. Activated $N_2$ molecules

$N_2 + e \rightarrow N_2^* + e$

Cascade processes

$C^1\Pi_u \rightarrow \pi^2\Sigma_g \rightarrow \pi^2\Pi^\prime$  

$N_2^*$ Life time(s) Energy(eV)

$C^1\Pi_u$ 3.2 x 10$^{-8}$ 11.0

$\pi^2\Sigma_g$ 1.7 x 10$^{-6}$ 7.2

$\pi^2\Pi^\prime$ 2.0 6.2

The average time between collisions (atma) 10$^{-8}$-10$^{-9}$ s

The dissociative energy of $O_2$ molecule 5.1 eV

$N_2(A^3\Pi_u^*) \rightarrow N_2(x^3\Sigma_g^+) \frac{k_{(14)}(14)}{k_{(14)}^*} \rightarrow 2N(2^3P, 4^3S)$  

$k_{(14)}^* = 2.6 \times 10^{-10}$ cm$^3$ s$^{-1}$  

$k_{(14)} = 5.1 \times 10^{-10}$ cm$^3$ s$^{-1}$  

Lavren (1978)

$N_2(A^3\Pi_u^*) + O_2 \rightarrow k_{(6)-(11)}(6)-(11)$ Products

$k_{(6)-(11)} = 1.2 \times 10^{-12}$ cm$^3$ s$^{-1}$  

$N_2(A^3\Pi_u^*) + O_2 \rightarrow k_{(6)-(11)}(6)-(11)$

$N_2(A^3\Pi_u^*) + O_2 \rightarrow k_{(6)-(11)}(6)-(11)$

$N_2(A^3\Pi_u^*) + O_2 \rightarrow k_{(6)-(11)}(6)-(11)$

$N_2(A^3\Pi_u^*) + O_2 \rightarrow k_{(6)-(11)}(6)-(11)$

Fig. 1 The ozone efficiencies in each $O_2$ mole fraction.

dashed line (a)  effective ozone efficiency

solid line (b) ozone efficiency without SF$_6$

solid line (c) maximum ozone efficiency with SF$_6$
Table 5. The branching ratio of Reactions (4) to (12)

\[
\begin{array}{llll}
\text{[O}_3\text{]}/([\text{O}_2]+[\text{N}_2]) & \text{SF}_6 / \% & (6) \rightarrow (7) / (8) : (12) \\
0 & 91.9 & 1.9 & 6.2 \\
0.05 & 0.08 & 93.4 & 1.9 & 4.7 \\
0.1 & 0.1 & 92.4 & 1.9 & 5.7 \\
0.2 & 0.08 & 92.5 & 2.0 & 2.5 \\
0.1 & 0.1 & 95.9 & 2.0 & 2.1 \\
0.2 & 0.05 & 96.3 & 2.0 & 1.7 \\
0.1 & 0.08 & 95.3 & 2.0 & 2.7 \\
\text{glass wool 3g} & 84.0 & 0.9 & 14.1 \\
0.4 & 0.25 & 90.7 & 0.9 & 7.4 \\
0.05 & 0.05 & 97.3 & 2.0 & 0.7 \\
0.0 & 0.01 & 93.3 & 1.9 & 4.8 \\
0.025 & 0.025 & 97.5 & 2.0 & 0.5 \\
\end{array}
\]

Fig. 3
The solid lines show O₃ formation vs discharge current and the dashed lines show NOₓ formation vs discharge current when the gap separation changed from 1mm to 3mm. The slopes show the ozone and NOₓ current efficiency.

Fig. 2
NH₃ formation vs discharge current when the gap separation changed from 1mm to 3mm. The slope shows the NH₃ current efficiency.

Fig. 4
The rising ratio of O₃ and NOₓ current efficiency by the addition of SF₆ in each O₂ mole fraction.