Increasing the Concentration of Singlet Delta Oxygen in Discharge Products by Adding NO\textsubscript{2} to Oxygen

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Abstract—The possibility is considered of increasing the concentration of singlet oxygen (SO), which is obtained in a discharge, by way of adding nitrogen dioxide to the starting gas. The presence of NO\textsubscript{2} in the mixture must cause the removal of atomic oxygen formed in the discharge and, accordingly, a decrease in the loss of SO. The simulation of the kinetics of the products of dc discharge in a flow of oxygen is used for determining the values of expected increase in the concentration of SO, as well of the concentration of NO\textsubscript{2}, which are required for attaining the maximal effect. It is demonstrated that, at oxygen pressures of ~6 torr and higher, the addition of NO\textsubscript{2} may produce a double and higher increase in the concentration of SO in regions of post-discharge flow with transport times of ~5–10 ms.

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INTRODUCTION

Intensive investigations are under way in present of the physical processes of production and loss of singlet delta oxygen (SO) in electric discharges. Considerable interest is aroused by the problem of developing an SO generator for oxygen-iodine laser [1–5]. Theoretical models of kinetics of discharge plasma components and post-discharge products, which take into account the known physicochemical processes, reveal that fairly high concentrations of SO may be attained under certain conditions in oxygen and its mixtures such as O\textsubscript{2}: Ar or O\textsubscript{2}: He. However, the experimentally obtained concentrations of SO often turn out to be lower than their predicted values. Apparently, significant impact is made in reality by some processes which are not included in the models.

Early models [6–9] did not include the three-particle process

\[ \text{O}_2(^1\Delta) + \text{O} + \text{O}_2(\text{X}) \rightarrow 2\text{O}_2(\text{X}) + \text{O}, \]

which still remains to be studied. The following obvious reasoning favors the existence of this process. Well known is the process

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

with the rate constant \( k_2 = 6 \times 10^{-34} \text{ cm}^6/\text{s} \) at \( T = 300 \text{ K} \) [10]. It is known that three-particle processes occur in two stages. In the first stage, an intermediary excited short-lived state is formed: in our case, that of \( \text{O}_2^* \) triatomic molecule. Then the molecule in the excited state gives up excess energy on colliding with the third particle. The interaction of oxygen atom with the electron-excited state \( \text{O}_2(^1\Delta) \) of \( \text{O}_2(\text{X}) \) molecule rather than with this molecule proper apparently does not rule out the possibility of formation of an analogous short-lived complex \( \text{O}_2^* \). In so doing, excess energy may be both released to the third particle and spent for dissociation according to process (1).

Process (1) was assumed by Vasiljeva et al. [11], who assumed its rate constant \( k_1 \) to have the value of \( 1 \times 10^{-32} \text{ cm}^6/\text{s} \) obtained from estimates and from comparison of the results of calculation of the kinetics of SO and the experimental results. The same team of researchers later cited the value of \( k_1 = (2 \pm 1) \times 10^{-32} \text{ cm}^6/\text{s} \) [12]. Based on the foregoing, we likewise included process (1) into the model of kinetics of steady discharge plasma components in a flow of oxygen, and the constant \( k_1 \) was taken to be the variable parameter. With \( k_1 = k_2 \), the calculations revealed a slight effect of process (1) on the concentration of SO. The values of \( k_1 = (0.3–1) \times 10^{-31} \text{ cm}^6/\text{s} \) brought about a much better agreement between the simulation [13] and experimental [14] results.

The rate constant \( k_1 \) was recently determined in direct experiments involving the measurement of the times of deactivation of \( \text{O}_2(^1\Delta) \) molecules in the presence of oxygen atoms and \( \text{O}_2(\text{X}) \) molecules with concentrations \( [\text{O}_2(\text{X})] \sim 2 \times 10^{19} \text{ cm}^{-3} \) [15]. The value of \( k_1 = 1.1 \times 10^{-31} \text{ cm}^6/\text{s} \) at temperature \( T = 300 \text{ K} \) was obtained.

Previously, the significant impact made by oxygen atoms on the concentration of SO in discharge products at pressures above 10 torr was experimentally demonstrated [16, 17]. In these studies, provision was made for removing oxygen atoms from post-discharge prod-
ucts; for this purpose, HgO plates were placed into the channel of flow after the discharge. The introduction of HgO resulted in a significant decrease in the rate of loss of O$_2$($^1\Delta$) molecules. Their concentration increased in the channel downstream behind the region of removal of oxygen atoms. The disadvantage of the method of removing oxygen atoms using HgO consists in the use of mercury which is ecologically hazardous. In addition, certain limitations may apparently be associated with the heterogeneity of this process of removal of atoms.

It is the objective of our study to demonstrate that the concentration of SO in discharge products in a flow of oxygen may be increased by way of adding nitrogen dioxide NO$_3$ into the gas mixture and thereby removing oxygen atoms in homogeneous process. For this purpose, the simulation of kinetics of discharge products is used to determine the values of expected increase in concentration of SO, as well as of the concentration of NO$_2$ required for this.

MECHANISM OF INFLUENCE
AND MODEL OF KINETICS

The addition of NO$_3$ into the starting gas must have a significant impact on the concentration of SO on condition of existence of a strong mechanism of loss of O$_2$($^1\Delta$) molecules, associated with the presence of oxygen atoms in discharge products. We will assume that process (1) exists and that its rate constant has a value in accordance with [15]. We will consider the variation of concentration of SO which may be produced by the addition of NO$_2$ to the starting gas in the case of dc discharge in a flow of oxygen. The mechanism of removal of oxygen atoms using NO$_2$ is well known and used, in particular, in measuring the concentration of oxygen atoms by the method of titration. The basic process is

$$\text{NO}_2 + O = \text{NO}^* + O_2(X)$$

(3)

with the rate constant $k_3 = 6.5 \times 10^{-12}\exp(120/T) [10]$. The excited NO* molecules resulting from reaction (3) make a transition to the ground state due to spontaneous emission of photons. They may again form NO$_2$ molecules in the process

$$\text{NO} + O + O_2 = \text{NO}_2 + O_2,$$

$k_4 = 1 \times 10^{-31} (T/300)^{1.6} [10]$. (4)

A one-dimensional model of plasma-chemical kinetics was used in the calculations, which describes the variations along the flow of the concentrations of O$_2(X)$ molecules and particles of 19 types—electroneutral: O$_2$($^1\Delta$), O$_2$($^1\Sigma$), O$_2$(A$^3$), O$_2$(W), O$_2$(X, $v = 1–4$), O($^1P$), O($^1D$), O($^1S$), O, NO, NO$_2$—and ions: O$^+$, O$^-$, O$^+_2$, O$, O^+$. In the model, the reduced intensity of electric field $E/N$ and the electron concentration $n_e$ were calculated by voltage $U_d$ and by the discharge current, which were preassigned by the data of experiment involving pure oxygen. The field intensity $E$ was assumed to be constant along the current and was calculated by subtracting from $U_d$ the electrode potential drops, the sum of which amounts to $300 \pm 20$ V according to the available data. The variations of pressure, density, velocity, and temperature of gas along the flow under heating in the discharge were described by gasdynamic equations for ideal gas. The heat exchange with environment was ignored.

The interaction between plasma electrons and O$_2$(X) and O was described by 15 processes for which the cross sections are known [18, 19]. For inverse processes of deexcitation by electrons of the states O$_2$($^1\Delta$), O$_2$($^1\Sigma$), O$_2$(A$^3$), O$_2$(W), O$_2$(X, $v = 1–4$), O($^1D$), and O($^1S$), the cross sections were determined from the principle of detailed balancing. In addition, the cross sections for O$_2$($^1\Delta$) were found, as in the models of other authors, by shifting the cross sections for O$_2$(X) on the axis of energies by 0.977 eV, i.e., by the value of energy of excitation of the state O$_2$($^1\Delta$). The rate constants of the processes listed above as functions of E/N were calculated for the electron energy distribution function found by solving the Boltzmann kinetic equation in two-term approximation.

The model of kinetics includes 107 processes of interaction between heavy particles. The set of processes and their rate constants for oxygen plasma are borrowed from the literature; they are the same as those in [9, 11]. The probabilities of loss in heterogeneous processes for particles of three main types, namely, O$_2$($^1\Delta$), O$_2$($^1\Sigma$), and O(P), were preassigned for each channel region: in the region of discharge and electrode—for the recombination of atoms $\gamma_{R} = 3 \times 10^{-3}$; in the post-discharge regions—$1 \times 10^{-4}$; for quenching of O$_2$($^1\Delta$) molecules—$\gamma_{Q} = 1 \times 10^{-8}$ and $4 \times 10^{-8}$, respectively; for quenching of O$_2$($^1\Sigma$) molecules—$\gamma_{Q} = 0.01$ and 0.016. As distinct from [11], the model further includes the processes of quenching of O$_2$($^1\Delta$) molecules by O($^1S$) and O$_2$(A$^3$) particles, the rate constants of which (2 $\times 10^{-10}$ and 8.1 $\times 10^{-11}$ cm$^3$/s) were borrowed from the experimental results of Kenner and Ogryzlo [20]. The distribution of products over the channels for O$_2$(A$^3$) was taken according to [13]. The quenching by O($^1S$) and O$_2$(A$^3$) particles has an appreciable impact on the concentration of SO within the discharge region, where the rate of loss of O$_2$($^1\Delta$) molecules due to these particles may be up to 20% of the overall rate for all processes. Nevertheless, the impact made by NO$_2$ impurity varies little when these processes are omitted from the model. Preassigned at the discharge inlet was the concentration of NO$_2$, the variations of which were described by processes (3), (4), and NO + O$_2$ = NO$_2$ + O with the rate constant of 1.8 $\times 10^{-12}\exp(-1370/T)$ cm$^3$/s [10]. Other processes of inter-