Effect of electronegative impurities on the generation of ozone in air

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A self-consistent numerical model is used to investigate the effect of electronegative impurities on the ozone yield in a dielectric barrier discharge with a pulsed voltage supply, and the range of impurity concentrations giving a substantial (two- or threefold) increase in the ozone yield is established. Sulfur hexafluoride is considered as a representative component having strong electronegative properties. It is shown that a tiny admixture \( \text{SF}_6 \leq 0.1\% \) can have an appreciable effect on the characteristics of an ozonator. The calculations are compared with published experimental data and given an interpretation. © 1999 American Institute of Physics. [S1063-7842(99)00701-1]

INTRODUCTION

Because of wide-ranging practical applications for ozonators, the physico-chemical principles of ozone synthesis have now been well studied both experimentally and theoretically.\(^1\) However, the role of gaseous impurities, which can substantially affect the characteristics of an ozonator, has not been adequately investigated. Such impurities include gaseous pollutants, many of which have strong electronegative properties. At the present time there is much interest in the creation of devices in which the synthesis of ozone is combined with the removal of various toxic components from the air. At the same time, an ozone generator based on a dielectric barrier discharge is very sensitive to the composition of the mixture of gases in the discharge gap. In particular, this was noted in Ref. 2, where it was found that an admixture of \( \text{SF}_6 \leq 0.1\% \) can sharply (by a factor of 2–3) increase the ozone yield per unit charge passed through the gap. The case considered in Ref. 2 can often arise in practice in the purification of air to remove halogen-containing impurities, which are harmful components of the effluents from various industrial processes. Thus the investigation of ozone synthesis processes remains a topical problem.

MODEL

The efficiency of ozone formation in air in the presence of an electronegative impurity was studied using a self-consistent numerical model for an ozonator operating in the single-pulse mode in dry air. The modeling was done for a gap with one dielectric electrode. The parameters of the gap were as follows: thickness of the dielectric 1 mm (\( \varepsilon = 4 \)), length of the air gap 2 mm, air temperature 293 K. Sulfur hexafluoride \( \text{SF}_6 \) was chosen as a representative component having pronounced electronegative properties. In the model it was assumed that the discharge channel is cylindrical, with a uniform distribution of particles over the volume. Such an approach is often encountered in the analysis of plasma-chemical processes in reactors based on barrier discharges.\(^1\)

In the calculation we used a set of 200 different reactions that occur in a plasma during and after the burning stage of the discharge and involve the participation of charged particles, excited molecules, atoms, and radicals. The rate constants of the elementary processes involving electrons were calculated on the basis of a numerical solution of the Boltzmann equation. A single-pulse mode was considered, when the ozone concentration is low and its synthesis is not influenced by processes involving the production of other components. In the calculations we used values for the rate constants of gas-phase reactions from Ref. 3 and 4 and the data of Ref. 5 and 6 on the cross sections for the interaction of electrons with molecular nitrogen and oxygen. The results of the modeling were compared with the experimental data.\(^1\)–\(^3\)

In the first stage of the modeling the results of the calculations were compared with the results of the known experimental papers on the synthesis of ozone in oxygen and in air. Such parameters as the amplitude of the current pulse, the energy characteristics, and the ozone yield were compared. The best agreement (\( \pm 30\% \)) was obtained for ozonators based on a barrier discharge with a pulsed voltage supply.\(^1\) The discrepancy is apparently due to the fact that in all the calculations the shape of the supply voltage pulse was specified as square. The agreement of the calculation with the experimental results of Ref. 2, in which an ozone generator with a pulsed voltage supply was also used, turned out to be not as good.

Figure 1 shows an example of the calculation of the ozone yield in a self-sustaining discharge for pure air as a function of the energy deposition in the single-pulse mode. At large energy depositions there is a simultaneous increase in the expenditure on the synthesis of the \( \text{O}_3 \) molecule and an increase in the fraction of oxides of nitrogen. At low energy depositions and short durations of the discharge pulse the
efficiency of the reactor approaches the theoretical limit, but here there is a noticeable increase in the production of NOX.

At the same time, for pure oxygen the field in a self-sustaining discharge is close to optimal in terms of the parameter E/N (E is the electric field and N is the density of particles), and therefore the expenditure on the formation of O3 is less dependent on the operating regime of the apparatus.

ELECTRONEGATIVE IMPURITIES IN AIR

The influence of an SF6 impurity on the operation of an ozonator was investigated experimentally in Ref. 2, where a single-pulse mode of excitation of the of a barrier-discharge cell was used. Since only the current was recorded in the experiment, the O3 yield per unit charge passed through the gap was determined from it. The change in the ozone concentration with time was measured from the absorption of ultraviolet radiation from a mercury lamp with wavelength λ = 254 nm. For single-pulse excitation a small concentration of atomic oxygen O was formed in the reactor; this atomic oxygen is then almost totally used up in the formation of O3. Other components that might appear following reactions of O3 with other gases are capable of influencing the ozone formation process in the reactor are practically absent. This allows one to study experimentally the influence of various impurities on the kinetics of ozone synthesis. For example, in the given experiment it was found that a tiny concentration of SF6 (less than 0.5%) can materially increase the O3 yield per unit charge passed through the barrier-discharge cell in a single pulse.

Figure 2 shows, in relative units, one of the dependences (η/η0) that can be affected by an SF6 mixture. Here η is the ozone yield per unit charge, η is the energy efficiency of its formation, and η/η0 is the energy efficiency in relative units (η0 and η are the O3 yields in pure air). The data points in Fig. 2 correspond to the SF6 concentrations chosen in the experiment. In the calculation one additional value was taken, for 2% SF6. It should be noted that the ratio η/η0 changes more sharply in the experiment than in the calculation. A probable reason for this is the difference in the shape of the supply voltage pulse. The ozone yield η0 in the experiment is larger than that corresponding to the case of a sinusoidal supply voltage of the discharge cell.

In addition, as we see from Fig. 2, the calculated energy efficiency varies less substantially than in the experiment. These two features can be explained by Fig. 3, which shows the charge Q that has passed through the cell, the energy deposition W, the ozone concentration [O3], and the parameter E/N as functions of the SF6 content. We see that at first there is a sharp decrease in Q on account of a decrease in current (Fig. 4); the ratio of its decrease in relative units is considerably higher than the rate of decrease of the energy deposition. The ozone concentration at the output initially varies little (this is due to an increase in the field in the discharge channel and an increase in the efficiency of O3 generation). As E/N approaches the optimum value for air, the further growth of η slows down, and the ozone concentration begins to fall off. When the SF6 concentration is increased above 1% the value of η even decreases somewhat. The authors of Ref. 2 attribute this to quenching by the SF6 molecule of the excited levels of nitrogen, which actively participate in the oxygen dissociation reactions. A calculation shows (Fig. 5) that SF6 does indeed lower the efficiency of the reactor approaches the theoretical limit, but here there is a noticeable increase in the production of NOX.