The effect of temperature on electron recombination with water and hydrocarbon ions in high-voltage nanosecond discharge afterglow

M.A. Popov[1], A.Yu. Starikovskiy[2], I.V. Kochetov[3], and N.L. Aleksandrov[1]

[1]*Moscow Institute of Physics and Technology, Dolgoprudny, Russia*
[2]*Princeton University, Princeton, USA*
[3]*SRC RF Troitsk Institute for Innovation and Fusion Research, Troitsk, Russia*

Abstract: The results of the experimental study of high-voltage nanosecond discharge plasma in water vapor with nitrogen and oxygen and in hydrocarbon-containing mixtures were presented. The gas temperature ranged from 300 to 700 K and the gas pressure ranged from 2 to 10 Torr. Time-resolved electron density and the effective recombination coefficients were obtained. Their values were significantly decreased with increasing gas and electron temperatures.

Keywords: electron-ion recombination, cluster ions, high-voltage nanosecond discharge.

1.Introduction

Non-equilibrium discharge plasmas generated in water vapor, humid air and other H_2O-containing mixtures are important for atmospheric electricity and discharge applications. Water vapor plasmas are used in technology, with applications ranging from air purification to plasma medicine. Water vapor formation during plasma-assisted fuel oxidation also affects plasma properties in combustible mixtures [1]. Non-equilibrium discharge plasmas generated in gaseous hydrocarbons play an important role in plasma chemical film deposition and synthetic diamond deposition. Electron recombination with hydrocarbon ions is an important mechanism for electron loss and for chemically active species production in plasma-assisted ignition and combustion.

To simulate plasma properties, the rate coefficients for elementary reactions, including the processes controlling the production and the loss of charged particles, are required. Available data on the rate constants for recombination and ion conversion processes in water vapor and hydrocarbon plasmas are not complete [2]. Some rate constants vary greatly with increasing gas temperature. Therefore, it is important to study plasma properties at elevated temperatures in order to obtain information about the rates of elementary reactions with water vapor and hydrocarbon ions.

2.Experiment

In this work, the plasma decay was experimentally studied in pure hydrocarbons (CH_4, C_2H_6, and C_3H_8), hydrocarbon:O_2, O_2:H_2O and N_2:H_2O mixtures for gas pressures 1-7 Torr and gas temperatures 300-630 K. The rates of plasma recombination depend on the positive ion composition that is dominated by cluster ions for 300 K, whereas simple molecular ions are more important at gas heating. The rates of electron recombination for cluster ions are an order of magnitude greater than the rates for simple molecular ions [2].

In this work uniform plasma was generated using a high-voltage nanosecond discharge that developed in a gas in the form of a fast ionization wave. The discharge was initiated in a quartz tube with an inner diameter of 42 mm. The high-voltage cone electrode and the grounded ring electrode were separated by a distance of 90 cm. The discharge was ignited by 15 kV pulses (in the coaxial cable). The pulse full width at half maximum (FWHM) and the pulse rise time were 25 ns and 5 ns, respectively. Electron density was measured in the middle of the discharge gap during the discharge afterglow using a microwave interferometer with a wavelength of 3 mm.

Nichrome wires were reeled up on the quartz tube to heat the gas in the discharge gap. The temperature of the tube surface was measured by a thermocouple. The temperature inside the tube was numerically calculated using the measured temperature on the discharge surface. The energy deposited during the discharge pulse was not enough for additional gas heating, whereas the electron energy in the discharge phase was as large as 10 eV. Electrons were thermalized in the discharge afterglow. Calculations showed that the time of electron thermalization was much shorter than the time of the plasma decay in the molecular mixtures studied. It may be concluded that the plasma decayed when the electron temperature was equal to the gas temperature T. In addition, the mixtures were diluted with Ar to retard electron thermalization and to study the effect of electron temperature on plasma recombination.

3.Results and discussion

Fig. 1 shows the measured time-resolved electron density for O_2:H_2O mixtures at T = 300 and 630 K. From this figure, the heated plasma decayed much slower than did the plasma for room temperature. The time it takes to halve the electron density was 0.6 µs for 300 K and 3.7 µs for 630 K. Similar observations were obtained in N_2:H_2O mixtures. Fig. 2 shows the similar measured results for pure ethane (C_2H_6) at T = 300 and 630 K. Similar observations were obtained in other pure hydrocarbons. It follows from our observations that the effect of gas temperature on the rate of hydrocarbon plasma decay is much less profound than that in H_2O-containg plasma decay.

There are three possible reasons for the decrease of the plasma decay rate with increasing T. Firstly, the electron-ion recombination coefficient α depends on T as $\alpha \sim T^{-m}$, where $m \sim 0.5$. This leads to a decrease in the rate of plasma decay only by a factor of ~1.4, much smaller than the decrease in the measured rates in H_2O-containg plasma when T was increased from 300 to 630 K. The factor of 1.4 was close to the accuracy of our electron density measurements.

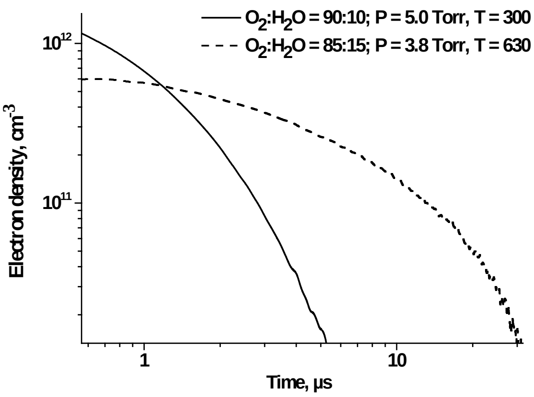

Fig. 1. Evolution in time of electron density during the plasma decay in O_2:H_2O mixtures.

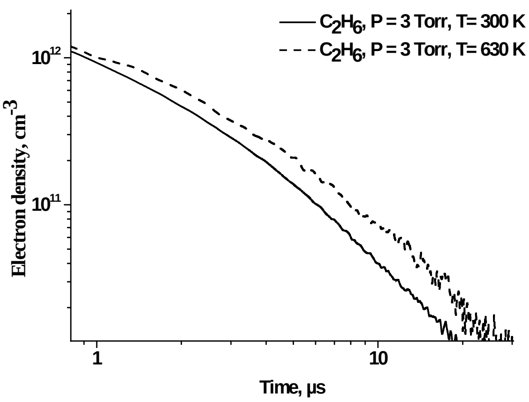

Fig. 2. Evolution in time of electron density during the plasma decay in C_2H_6.

Secondly, cluster ions were formed via three-body conversion reactions $A^+ + B + M \rightarrow A^+(B) + M$, whereas other reactions were binary ones. Therefore, the composition of cluster ions and the effective recombination coefficient depended on the gas number density N that changed with gas temperature and pressure p as $N \sim p/T$ (the equation of state for an ideal gas). To demonstrate this effect, Fig. 3 compares the effective recombination coefficients for various values of T, whereas the values of p were selected such that the values of N were almost the same. The comparison was made for the plasma decay in pure C_2H_6 and in the N_2:H_2O mixtures. The values of α were determined from the equation

$$1/n_e(t) = 1/n_e(0) + \alpha t, \quad (1)$$

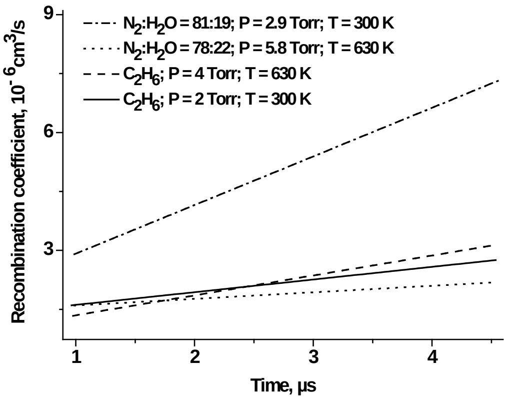

Fig. 3. Evolution in time of the effective recombination coefficient during the plasma decay.

where $n_e(t)$ is the measured electron density and $n_e(0)$ is its initial value. It follows from Fig. 3 that the coefficient α is almost independent of T at N = const for the C_2H_6 plasma. However, the influence of gas temperature on the value of α is obvious in H_2O-containing mixtures even at N = const. This is explained by the third reason that the plasma decay rate decreases with increasing T. This reason is a temperature dependence of the rates for the conversion of simple ions to cluster ions. For water vapor ions, this reaction is [3]

$$H_3O^+(H_2O)_n + H_2O + M \rightarrow H_2O^+(H_2O)_{n+1} + M. \quad (2)$$

For instance, the rate coefficient for this reaction at n = 0 is $k = 3.2\times10^{-27}(300/T)^4$ cm^6/s [3]. To demonstrate this, we simulated the plasma decay in H_2O-containing mixtures under the conditions considered using available data on the rate constants [3, 4]. A system of balance equations for electrons and ions was numerically solved in a zero dimensional approximation. Fig. 4 compares the calculated electron density histories during the plasma decay in a O_2:H_2O = 3:1 mixture with the measured data. Good agreement was obtained for T = 630 K. Calculations show that here the plasma decay was dominated by electron recombination with O_2^+ ions formed in the $H_2O^+ + O_2 \rightarrow H_2O + O_2^+$ reaction. At room gas temperature the dominant ion species were $H_3O^+(H_2O)_n$ ions [4], whereas at T = 630 K the ion composition was dominated by H_2O^+ and H_3O^+ ions (see Fig. 5).

The time-resolved electron density was also measured in the afterglow of a high-voltage nanosecond repetitively pulsed discharge in hydrocarbon:O_2 mixtures at gas temperatures from 300 to 630 K. At 300 K, the effective recombination coefficient changed nonmonotonously when the number of voltage pulses and the oxidation degree increased, by analogy with [5]. The measured results for 630 K show (see Fig. 6) that the effect of gas temperature is not reduced to the effect of gas density in combustible mixtures. In this case, the peak value of the recombination coefficient changed nonmonotonously when the number of voltage pulses and the oxidation effective recombination coefficient decreases with increasing *T*. It may be concluded that the nonmonotonous dependence of the recombination rate is associated with the presence of cluster ions with the fraction that decreases when the gas is heated.

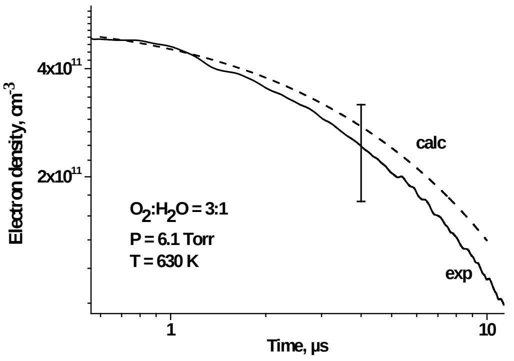

Fig. 4. Measured and calculated evolution in time of electron density during the plasma decay for 630 K.

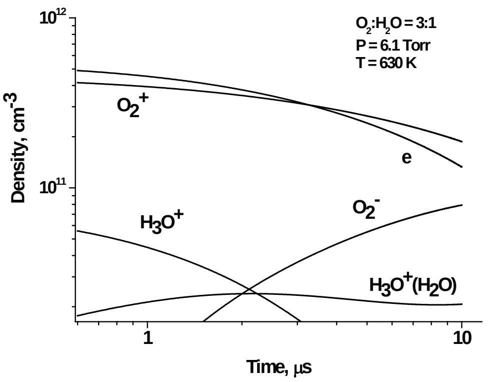

Fig. 5. Evolution in time of electron and ion densities during the plasma decay for T=630 K.

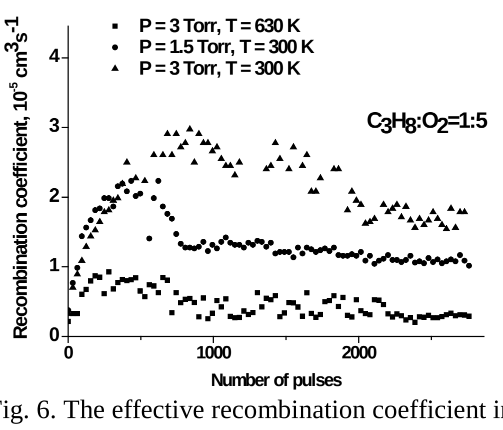

Fig. 6. The effective recombination coefficient in a C_3H_8:O_2 = 1:5 mixture afterglow versus the number of voltage pulses.

Dilution of the mixtures studied with Ar led to a decrease in the rate of plasma decay. Numerical analysis showed that this was associated with a slow electron thermalization. As a result, the plasma decayed at elevated electron temperatures at which the recombination coefficients were reduced.

4.Conclusions

In summary, it was experimentally observed that an increase in gas temperature from 300 to 630 K and an increase in electron temperature led to a decrease in the rate of plasma decay for gas plasma in pure hydrocarbons and in hydrocarbon:O_2, O_2:H_2O and N_2:H_2O mixtures. The effect of gas temperature on the effective recombination coefficients in the hydrocarbon plasmas was induced only by the change in the composition of cluster ions due to gas number density variation. The effect of gas temperature on the effective recombination coefficients in the O_2:H_2O and N_2:H_2O plasmas was much more profound and was mainly associated with a strong temperature dependence of the rates of water cluster ion formation. The decrease of the recombination coefficient in partially oxidized combustible mixtures seems also to be associated with less efficient production of cluster ions.

5.Acknowledgements

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6.References

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