

A chemical-kinetic model of DBDs in Ar-H₂O mixtures

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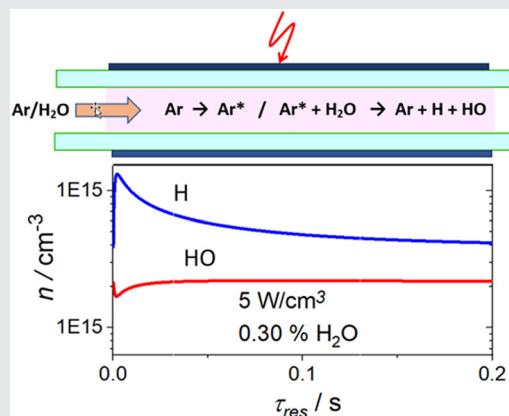
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Abstract

A simplified chemical-kinetic model was applied to Ar-H₂O dielectric-barrier discharges (DBDs), presuming that dissociation processes are only due to energy transfer from excited Ar species. Good agreement was obtained between the densities of HO, H₂, and O₂ and experimental data from the literature, whereas a discrepancy for H₂O₂ could not be explained. The model is useful for designing DBD reactors and process development. Steady-state densities of H atoms increase with decreasing fractions of x_{H₂O} which should be kept below 0.1% to obtain a large zone of virtually constant and large H-atom density in the DBD reactor, whereas the HO density is hardly affected by x_{H₂O}. O₂ contaminations must be kept well below 100 ppm in to attain maximum H-atom densities.



KEYWORDS

argon-water, dielectric-barrier discharges, hydrogen atoms, HO, radicals

1 | INTRODUCTION

In the past 15 years, the number of scientific publications on atmospheric pressure plasmas in mixtures of argon and water vapor has been increasing substantially, driven by a large number of potential applications in the areas of water purification, decontamination, surface treatment, as well as for biochemical and agrochemical or biomedical applications. The subject of the present paper emerged during an experimental study related to the application of dielectric-barrier discharges (DBDs) in humid argon for the cleaning and hydroxylation of fused silica as a pretreatment for a subsequent vapor-phase silanization, the results of which

are reported in an accompanying publication.^[1] The species of main importance for this application are strongly oxidizing hydroxy radicals, HO, and hydrogen atoms, H, which play a central role in removal of organic contaminants and for the rehydroxylation of dehydroxylated silica surfaces, respectively. The chemical-kinetic model outlined here was developed after the experimental study was largely completed, in an attempt to obtain information about the densities of HO and H achieved under the experimental conditions, to support designing of scaled-up DBD reactors, and to guide further process development for this application. One important result of the model calculations, the finding that decreased water vapor

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fractions $x_{\text{H}_2\text{O}}$ in the feed gas result in higher H densities, then motivated additional silanization experiments which are also reported in Reference [1].

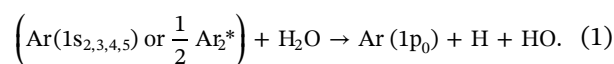
2 | GAS-PHASE CHEMISTRY OF AR-H₂O DBDS

Due to their interest for a wide range of applications, studies on atmospheric pressure plasmas in water-containing gas mixtures have been reported in a large number of papers during the past 15 years (see, for example, References [2–11] and papers cited therein). Comprehensive plasma-chemical-kinetic models have been developed in several of these publications. In the present paper, a strongly simplified approach is applied to get an idea of spatially averaged densities of reactive species like H atoms, HO radicals, ozone, and hydrogen peroxide in mid-frequency DBDs in humid argon, and of the dependence of these densities on experimental parameters like power density, residence time, and water vapor mole fraction, $x_{\text{H}_2\text{O}}$. This approach follows the concept outlined in a recent paper on Ar-HMDSO mixtures.^[12]

Under typical conditions of a DBD in Ar containing only small mole fractions of a molecular gas like water ($x_{\text{H}_2\text{O}} < \text{about } 3\%$ at room temperature), more than 50% of the dissipated electrical energy is converted into excitation energy of the four lowest excited states of the Ar atoms, between 11.55 and 11.83 eV. At reduced fields typical of atmospheric pressure DBDs in Ar, these states, denoted—in Paschen nomenclature and in the sequence of decreasing energy—as Ar(1s_{2,3,4,5}), are generated in the ratios $g_2:g_3:g_4:g_5$ of about 0.40:0.05:0.26:0.29.^[13] At sufficiently high mole fractions $x_{\text{H}_2\text{O}}$ of water, energy transfer reactions between Ar atoms in these states and H₂O are virtually the only reaction channels of these species. A rate coefficient of $4.8 \times 10^{-10} \text{ cm}^3/\text{s}$ for quenching of Ar(1s₅) by H₂O was reported by de Jong^[14] and later confirmed by Leblond et al.^[15] In the absence of empirical or theoretical data, it appears reasonable to assume that the rate coefficients for quenching by water are not too different for other Ar(1s) levels, similar to what was observed for several other small molecules.^[16] For the reaction of the Ar excimer Ar₂(³Σ_u) with water, the rate coefficient is $14 \times 10^{-10} \text{ cm}^3/\text{s}$, three times larger than for Ar(1s₅).^[15] However, for water vapor densities beyond $1.6 \times 10^{16} \text{ cm}^{-3}$ ($x_{\text{H}_2\text{O}} > 0.07\%$), the participation of excimers will decrease below about 15% because increasing amounts of Ar(1s₅), from which the excimers are formed, will be quenched by water, see fig. 4 in Reference [12]. “Sufficiently high mole fractions” (see above) means that $x_{\text{H}_2\text{O}}$ is large enough to keep

alternative relaxation processes of Ar* at less than, say, 5%. (In the following, the symbol “Ar*” is used to symbolize a “lumped species,” representing the sum of excited Ar species, which are mainly contributing, thanks to a sufficient lifetime, to reactions with H₂O: Ar(1s) atoms as well as Ar₂(³Σ_u.) Assuming that the frequency of such processes as determined for Ar-HMDSO mixtures^[12] ($2.4 \times 10^5 \text{ s}^{-1}$) may also be applied here, the corresponding H₂O fraction is 500 ppm (0.05%).

Reactions between Ar* and water at atmospheric pressure result in dissociation of H₂O into H atoms and HO radicals as the only product channel (see equation below), whereas dissociation into two H and O has also been reported, in 46% of the reactions between H₂O and metastable Ar(1s) atoms, at pressures of a few Torr.^[15,17]



The total rate, g , by which the excited argon species, Ar*, are generated by electron collisions with Ar, $g = g_5 + g_4 + g_3 + g_2$, can be calculated from the solution of the stationary electron Boltzmann equation. Using the established multi-term method for the solution of this electron-kinetic equation^[18] and the electron-collision cross sections for argon reported in Reference [19], the result, including direct excitation as well as cascading from higher levels, is $g = 4.4 \times 10^{-17} \text{ cm}^{-3} \text{ s}^{-1}$ for pure Ar at 100 Td and a power density dissipated in the discharge of $p_V = 1 \text{ W}/\text{cm}^3$.^[20] This figure represents the rate of reaction A00 in Table 1,

TABLE 1 First reactions within the simplified model of Ar-H₂O dielectric-barrier discharge chemistry, with generation and decay of Ar*, reactions of Ar* with major stable species and H₂O₂, as well as recombinations between H and HO

R#	Educts	Products	k _#
A00	Ar	Ar*	$g = 4.4\text{E}17 p_V / (\text{W} \cdot \text{cm}^{-3}) / \text{cm}^3/\text{s}$
A0	Ar*	Ar (+hν)	2.4E5 s ⁻¹
A1	Ar* + H ₂	Ar + 2H	7E–11 cm ³ /s
A2	Ar* + H ₂ O	Ar + H + HO	4.8E–10 cm ³ /s
A3	Ar* + H ₂ O ₂	Ar + 2HO	2E–10 cm ³ /s
A4	Ar* + O ₂	Ar + 2O	2E–10 cm ³ /s
1	2H + Ar	H ₂ + Ar	1.8E–30 T ⁻¹ cm ⁶ /s
2	H + HO + Ar	H ₂ O + Ar	2.3E–26 T ⁻² cm ⁶ /s
3	2HO + Ar	H ₂ O ₂ + Ar	6.5E–31 (T/300) ^{-2.9} cm ⁶ /s

Note: See Table S1 for the full scheme and sources of rate coefficients.

featuring the first nine reactions from the complete scheme in Table S1 shown in the Supporting Information. Originally, it had been expected that this figure would still be representative for Ar-H₂O mixtures with a small water content, up to about $n_{\text{H}_2\text{O}} = 10^{17} \text{ cm}^{-3}$ ($x_{\text{H}_2\text{O}} \approx 0.4\%$). Experimentally, it has been reported in the literature, however, that increasing $x_{\text{H}_2\text{O}}$ from 0.25% to 2.5% has only a small impact on the densities of HO radicals, varying within a range of only $\pm 10\%$, with a flat maximum for $x_{\text{H}_2\text{O}} = 0.4\text{--}2.0\%$.^[7] As shown in Figure S1, the model presented here also results in very similar HO densities for the same range. Therefore, we are confident that reasonable results can still be obtained working with the same value of g for up to 1.7%. Even experimental results obtained with argon virtually saturated with water vapor at room temperature (fractions of stable products H₂ and O₂ at $x_{\text{H}_2\text{O}} = 3\%$) can be reproduced reasonably well with the same value of g as shown below.

For mole fractions decreasing well below about 0.05%, the reaction probability with water is expected to decrease because the Ar(1s) species will increasingly become deactivated by competing radiative and collisional processes. To take this into account, a water-independent decay reaction was included (reaction A0) using the same frequency as determined for DBDs in Ar-HMDSO.^[12]

3 | RESULTS AND DISCUSSION

For water mole fractions beyond 0.05%, the generation rate g virtually equals the rate at which H atoms and HO radicals are generated by the reaction A2 in a fresh gas entering the plasma zone. For short residence times, a rough estimation of concentrations n_{H} and n_{HO} may be attempted by equating the generation rates and three possible three-body recombination reaction rates of H and HO (entries R1, R2, and R3 in Table 1) which are their fastest reactions in the virtual absence of other radical or atomic species, dioxygen, or hydrogen peroxide:

$$d(n_{\text{H}})/dt \approx g - n_{\text{Ar}}n_{\text{H}}(k_1n_{\text{H}} + k_2n_{\text{HO}}) = 0, \quad (2)$$

$$d(n_{\text{HO}})/dt \approx g - n_{\text{Ar}}n_{\text{HO}}(k_2n_{\text{H}} + k_3n_{\text{HO}}) = 0. \quad (3)$$

The solutions of these equations ($n_{\text{H}} = 9.5 \times 10^{14} \text{ cm}^{-3}$, $n_{\text{HO}} = 9.1 \times 10^{13} \text{ cm}^{-3}$ for $p_{\text{V}} = 1.5 \text{ W/cm}^3$ at 300 K) are shown in Figure 1, together with the temporal evolution of eight species in a DBD with 0.3% water for a power density of 1.5 W/cm^3 at 300 K. For HO, there is a good agreement up to about 0.01 s, whereas for H, the quasi-steady state expressed by Equation (2) cannot be achieved before other reactions partner except HO have already gained too high densities to be negligible.

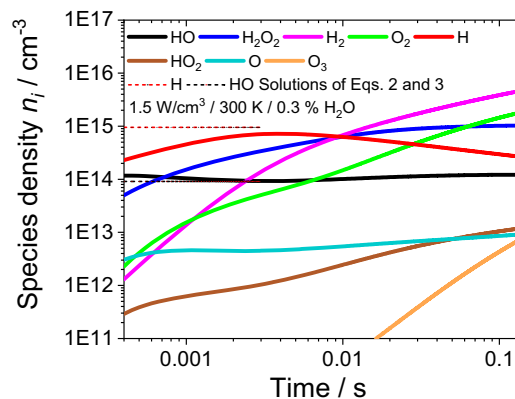


FIGURE 1 Time evolution of species in an Ar-H₂O dielectric-barrier discharge with 0.3% water, with a power density of 1.5 W/cm^3 at 300 K up to a residence time of 0.14 s. Gap width $d = 0.2 \text{ cm}$. The dotted horizontal lines indicate n_{H} and n_{HO} as obtained from Equations (2) and (3). Note that the ratio $n_{\text{H}_2\text{O}_2}/n_{\text{HO}}$ becomes nearly constant (≈ 9) for $t > 0.02 \text{ s}$

The time evolution of species densities shown in Figure 1 was obtained by integration of the rate equations derived from the set of 30 equations given in Table S1, using the CVODE solver option within the XPP software (University of Pittsburgh, Department of Mathematics, freely available). The chosen conditions ($x_{\text{H}_2\text{O}} = 0.3\%$, $p_{\text{V}} = 1.5 \text{ W/cm}^3$, $\tau_{\text{res}} = 0.14 \text{ s}$) are those used for most of the experimental results which were obtained before the present model was developed.^[1]

Wall recombination reactions were included in the rate equations of radical species, using wall loss times calculated after Chantry^[21,22] to check at which values of recombination probabilities an influence on the results became noticeable (i.e., larger than 5%). This was typically the case (for $d = 0.2 \text{ cm}$) for values of γ_i in the range of 0.01 (0.001 for H), due to fast gas-phase reactions. Results shown here were calculated with $\gamma_i = 1 \times 10^{-5}$ for all radicals, so that wall effects are virtually excluded.

To check the validity of the calculated results, a comparison was made with experimental data from studies in which comparable experimental parameters were applied. Surprisingly good agreement is obtained for the mole fractions of stable gaseous products H₂ and O₂ from DBDs in humidified Ar (>95% relative humidity^[2]; Figure 2a) and for the densities of HO radicals, measured in situ by optical absorption as a function of power densities^[7] (Figure 2b). The latter experimental results are virtually constant for water fractions $x_{\text{H}_2\text{O}}$ from 0.4 to 2.0%—an observation which may be considered characteristic for water dissociation mainly driven by reaction with energetic Ar species: The dissociation rate equals the rate at which energetic Ar species Ar* are generated, virtually independent of $x_{\text{H}_2\text{O}}$ in this range.

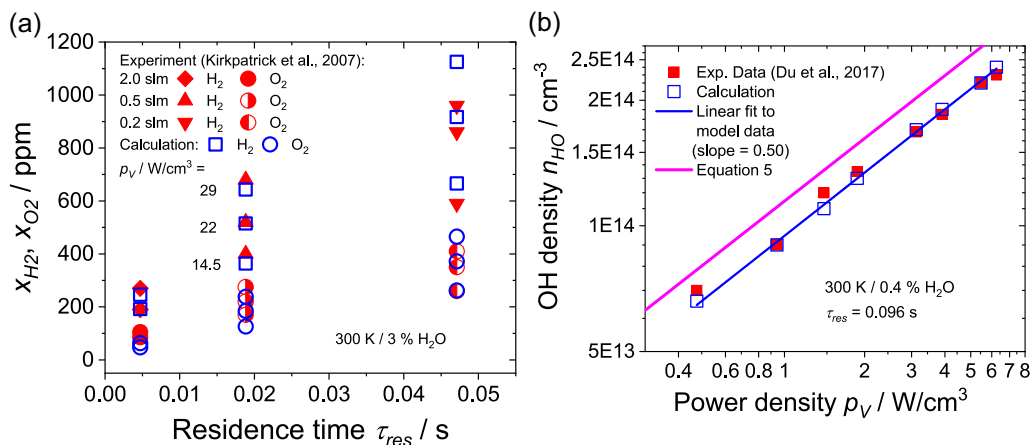


FIGURE 2 Comparison of model results with experimental data from the literature. (a) Mole fractions of H₂ and O₂ produced as a function of residence time for different power densities. Triples (for $\tau_{res} = 47$ ms: pairs) of data points correspond, top-down, to 29, 22, and 14.5 W/cm³, respectively. Data for 29 and 22 W/cm³ only are given for $\tau_{res} = 47$ ms. Experimental data.^[2] (b) HO densities as a function of power density ρ_V calculated for $x_{H_2O} = 0.4\%$ (time averages up to $\tau_{res} = 96$ ms). For $x_{H_2O} = 2.0\%$ results are only 2% larger. Experimental data^[7] are virtually the same for these two fractions. The red line was calculated with the aid of Eq. 5, see below

There is, however, also a significant discrepancy with both papers^[2,7] as far as the fraction of hydrogen peroxide, H₂O₂, is concerned: Du et al.^[7] found the ratio $n_{H_2O_2}/n_{HO}$ to be virtually constant at 1.3 for an order-of-magnitude variation of power and $x_{H_2O_2}$ was always <11 ppm for the parameters given in the legend of Figure 2a and remarkably independent of energy density beyond 0.2 J/cm³ deposited in the gas.^[2] The model calculation, by contrast, yields a virtually constant ratio $n_{H_2O_2}/n_{HO} = 9$ beyond $\tau_{res} = 0.01$ s, and $x_{H_2O_2}$ up to 50 ppm after 0.14 s. Nearly the same constant ratio (7...9) was also reported for a RF-DBD with $\tau_{res} = 0.2$ s and 10 W/cm³ for $x_{H_2O_2} > 0.1\%$.^[6] The model results may be rationalized by considering the main reactions for formation and destruction of H₂O₂: the three-body recombination of two HO radicals, R3, and the reaction between HO and H₂O₂, R7 (Table S1), respectively. Equating the rates of these two reactions results in an approximation for the ratio of H₂O₂ and HO: $n_{H_2O_2}/n_{HO} = k_3 \times n_{Ar}/k_7 = 9.2$ at 300 K. At present, the discrepancy between experiments and models cannot be resolved; possibly there is an efficient reaction at the surfaces in contact with the DBDs, not included in the model, by which H₂O₂ is destroyed. A further discussion of this issue is beyond the scope of this paper.

The outlined model is helpful in finding conditions under which an extended zone of virtually constant high densities of H and HO may be achieved in a DBD reactor. Figure 3 shows n_H and n_{HO} as a function of residence times, which may be converted to the position x in the DBD reactor along the gas flow direction, assuming a plug flow profile. The calculation, made for several different input water fractions between 0.03% and 3.0% and for two different values of power density, 1 and 5 W/cm³, shows that the fraction of

water vapor should be kept below 0.1% to largely avoid destruction of H atoms by reactions with O₂. Although n_H is increasing substantially over the investigated range of x_{H_2O} , n_{HO} stays virtually constant. It should be kept in mind that the model results for $x_{H_2O} < 0.07\%$ are less reliable for reasons outlined above: Increasing contributions of the Ar₂* excimer as well as of deactivation of Ar(1s₂), (Ar1s₄), and Ar₂* by radiation.

The maximum density of H atoms which may be obtained under steady-state conditions, obtained within, for example, 0.1 s for $x_{H_2O} = 0.03\%$, is mainly limited by reactions with O₂, H, HO, and HO₂. After 2 s, the densities of these four species are 7.9×10^{14} , 4.1×10^{14} , 1.0×10^{14} , and 5.8×10^{12} cm⁻³, respectively (see Figure S1). Rates of

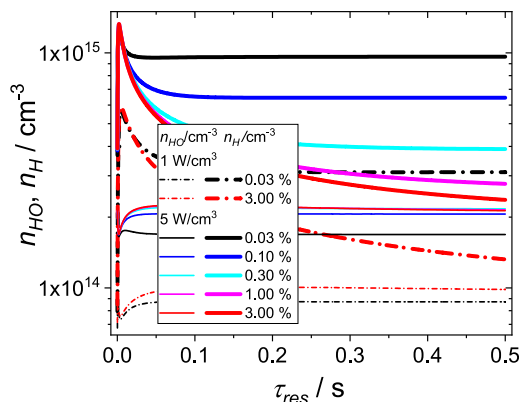


FIGURE 3 Densities of H atoms (bold lines) and HO radicals (thin lines) as functions of water vapor percentage for two different power densities. Note that the HO densities are virtually independent of $x_{H_2O} \geq 0.1\%$, whereas n_H increases steadily with decreasing x_{H_2O}

reactions between H and these species are calculated in the following equation:

$$\begin{aligned} & [(2 \times k_1 \times n_{\text{H}_2} + k_2 \times n_{\text{HO}} + k_{12} \times n_{\text{O}_2}) \times n_{\text{Ar}} \\ & + (k_8 + k_9 + k_{10}) \times n_{\text{HO}_2}] \times n_{\text{H}} \quad (4) \\ & = [115 + 634 + 340 + 464] \times 4.1 \times 10^{14} \text{ cm}^{-3} / \text{s} \\ & = 6.4 \times 10^{17} \text{ cm}^{-3} / \text{s}. \end{aligned}$$

Comparison of the results shows that the reactions with HO₂ and O₂, having strongly $x_{\text{H}_2\text{O}}$ -dependent densities, still contribute about 50% at $x_{\text{H}_2\text{O}} = 0.03\%$, whereas the rates for these decay channels increase rapidly with growing $x_{\text{H}_2\text{O}}$, resulting in the decline of n_{H} .

It is interesting to note that a simple approximate equation can be derived for the density of HO in the steady-state, by equating the rates of production in reaction A2 and of the main consumption reactions 3, 4, and 7, considering the virtual constant ratio $n_{\text{H}_2\text{O}_2}/n_{\text{HO}} = k_3 \times n_{\text{Ar}}/k_7$ (see above):

$$n_{\text{HO}} \cong \sqrt{g/(2 \times k_3 \times n_{\text{Ar}} + k_4)}. \quad (5)$$

Contribution by reaction (2) is neglected because n_{H} cannot be related to n_{HO} in a straightforward manner (see Equation 4). As shown in Figure S2, results of Equation (5) agree with figures calculated from the full model within a systematic error of at most +20% in the ranges of $1 < p_V/W \text{ cm}^{-3} < 10$ and $0.1 < x_{\text{H}_2\text{O}} < 3\%$ (see also the graph of Equation 5 in Figure 2b). For lower $x_{\text{H}_2\text{O}}$ the neglect of R2 results in larger errors due to growing densities of n_{H} (see Figures 3 and S1).

Another conclusion that may be drawn from the model is that the fraction of oxygen impurities in the reactor must be held well below 100 ppm to attain the highest possible H densities.

4 | CONCLUSIONS

The simplifying presupposition that dissociation processes are only due to energy transfer from excited Ar species (Ar atoms in 1s states as well as an Ar excimer), which are summarized as a “lumped species” Ar*, allows a straightforward description of chemical kinetics in an Ar-H₂O gas stream passing through a DBD zone. Good agreement was obtained with densities of HO, H₂, and O₂ reported in the literature. A major discrepancy was found, however, for the density of hydrogen peroxide, which so far was left unexplained. The model can be applied for the design of DBD reactors and to guide further process development. An important result of the model calculations was that the water mole fraction should be kept below 0.1% to obtain, in

the DBD reactor, a large zone of virtually constant and large H-atom density, whereas the HO density is hardly affected by variations of $x_{\text{H}_2\text{O}}$. From an analysis of model results, a simple equation was derived allowing a rough estimation of n_{HO} with a systematic error of at most +20% for a specified range of water vapor fractions and power densities. Finally, it may be concluded that O₂ contaminations must be kept well below 100 ppm to attain maximum H-atom densities.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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