

Plasma Chemistry of NO in Complex Gas Mixtures Excited with a Surfatron Launcher

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The plasma chemistry of NO has been investigated in gas mixtures with oxygen and/or hydrocarbon and Ar as carrier gas. Surface wave discharges operating at microwave frequencies have been used for this study. The different plasma reactions have been analyzed for a pressure range between 30 and 75 Torr. Differences in product concentration and/or reaction yields smaller than 10% were found as a function of this parameter. The following gas mixtures have been considered for investigation: Ar/NO, Ar/NO/O₂, Ar/NO/CH₄, Ar/CH₄/O₂, Ar/NO/CH₄/O₂. It is found that NO decomposes into N₂ and O₂, whereas other products such as CO, H₂, and H₂O are also formed when CH₄ and O₂ are present in the reaction mixture. Depending on the working conditions, other minority products such as HCN, CO₂, and C₂ or higher hydrocarbons have been also detected. The reaction of an Ar/NO plasma with deposits of solid carbon has also been studied. The experiments have provided useful information with respect to the possible removal of soot particles by this type of plasma. It has been shown that carbon deposits are progressively burned off by interaction with the plasma, and practically 100% decomposition of NO was found. Plasma intermediate species have been studied by optical emission spectroscopy (OES). Bands and/or peaks due to N₂^{*}, NO^{*}, OH^{*}, C₂^{*}, CN^{*}, CH^{*}, or H^{*} were detected with different relative intensities depending on the gas mixture. From the analysis of both the reaction products and efficiency and the type of intermediate species detected by OES, different plasma reactions and processes are proposed to describe the plasma chemistry of NO in each particular mixture of gases. The results obtained provide interesting insights about the plasma removal of NO in real gas exhausts.

I. Introduction

The abatement of NO present in exhaust gases resulting from combustion sources is a problem of great concern because of its deleterious effects on the environment. Typical processes for removal of NO_x are based on the use of catalysts.¹ Recently, the incorporation of plasma techniques has opened alternatives for NO_x removal, which, for certain niches of application could be an interesting and viable technology.^{2–5} Particularly, plasma processes can be of interest when the volume of gases is small (e.g., exhaust gases produced by mobile combustion sources) and the associated energetic costs are not a critical restriction.⁶ However, although much work has been dedicated during the past decade to the study of NO decomposition processes using plasmas,^{7–17} the abatement technology under real conditions is not completely mature. Besides the complexity of the plasma processes and their dependence on the actual experimental parameters that control the ignition of plasma and its stabilization, much work is still necessary to describe the plasma reactions that occur for the complex compositions of real exhausts. NO decomposition has been studied for plasmas ignited by different methods such as dielectric barrier processes^{2,7–9,11,12,16–19} corona or high voltage discharges,^{6,10,19–22} hollow cathode,¹³ pulsed microwave reactors,^{23–28} etc. However, most of these studies have addressed the decomposition reactions of NO in simple mixtures with other gases such as O₂ and/or N₂ or CO₂.^{2,7–9,12,13,16,23–28} By contrast, real exhaust gases are

complex mixtures whose exact composition depends on the type of combustor or motor. Thus, for example, diesel motors yield a complex gas mixture where NO_x is accompanied by other gases such as O₂, hydrocarbons, CO₂, H₂O, and solid particles of soot.^{6,9,14,21,22,29} The prediction of the plasma behavior with such a complex gas inlet is not easy, and many studies are still necessary to control the plasma chemistry under those conditions.

The present paper aims to study the plasma chemistry of mixtures of NO with CH₄ and/or O₂ by using nonequilibrium plasmas generated by traveling surface waves. Surface wave (SW) discharges operating at microwave frequencies have a flexible operation and are characterized by high densities of long-living and active species such as ground state atoms and excited particles and molecules in metastable and excited vibrational states. The plasma chemistry is strongly influenced by the degree of molecular dissociation due to the highly nonlinear collisional reactions occurring simultaneously in the bulk plasma and at the plasma–wall interface. These nonequilibrium processes strongly affect the whole discharge kinetics. SW sustained molecular plasmas are rather complex because the wave-to-plasma power transfer along the wave path is inhomogeneous. However, investigations with traveling SWs are motivated by the versatility of these sources compared with other plasma based technologies. For this preliminary study with a SW device we have used Ar as a carrier gas and looked to the plasma reactions taking place for mixtures of NO with O₂, (O₂ + N₂), CH₄, and (O₂ + CH₄), where the concentration of the minority components varies around the values existing in real exhausts. From a theoretical point of view, the understanding of the physics and chemistry working in discharges operating

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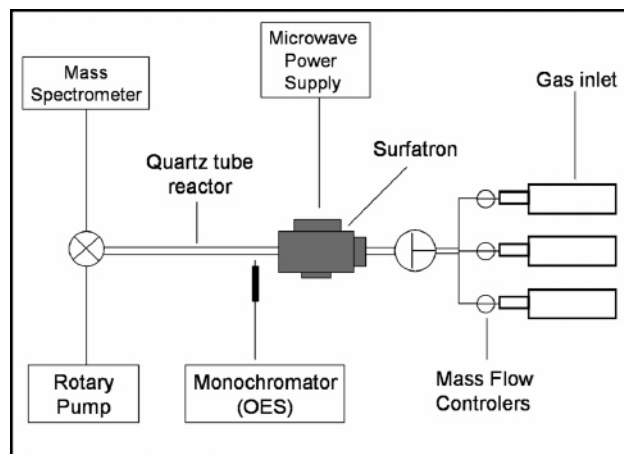


Figure 1. Scheme of the experimental setup used to decompose NO by microwave surface-wave plasma reactions from complex gas mixtures.

with such highly excited molecular gas mixtures is less advanced than the knowledge of discharges in pure molecular gases. Along the present study, it has been also shown that, depending on the relative concentration of O_2 and CH_4 in the mixture, carbon can be formed by plasma decomposition of methane. The formation and removal of carbon through different plasma reactions has provided useful clues to model the possible effect of plasmas on the particles of soot emitted from diesel engines, a process from which very few published works are available in the literature.^{6,29,30} In this work, the plasma is ignited and maintained with a surfatron as a SW launcher. This type of device is small and simple to operate and has been previously used for removal of VOCs (volatile organic compounds) and other noxious compounds.^{29–33} The pressure range selected for the present study has been limited to values comprising between 30 and 75 Torr. These working conditions are far from those existing in real exhausts, but the obtained results may provide useful clues to understand the basic processes of plasma reactions with complex mixtures of gases. The study of the reaction processes has been complemented by optical emission spectroscopy (OES) and the data have provided interesting information about the type and relative concentration of the intermediate species formed in each case.

II. Experimental Section

A scheme of the experimental setup is shown in Figure 1. The plasma reactor consists of a quartz tube of 3.5 mm inner diameter and 40 cm length. A typical glow length of approximately 4 cm was observed in most experiments. A surfatron is used to induce SW plasma. Microwave power is transported from the power supply to the surfatron via a coaxial cable coupled with a slot antenna directly connected to the surfatron.³⁴ Microwave power of 60 W was used in the experiments. Although this parameter was not modified for the series of results reported here, it is interesting to mention that very similar results were also obtained for smaller powers up to 20 W when the plasma extinguished. This yields an approximate energy density of 50–160 W/cm³. The gas mixtures are prepared with mass flow controllers connected to the entrance of the quartz tube. The Ar mass flow was between 25 and 50 sccm. Typical compositions of gas mixtures were as follows: carrier gas Ar, NO (3000 ppm), O_2 (from 0 to 5% in volume), CH_4 (from 0 to 5000 ppm). The flow of Ar was fixed at either 25 or 50 sccm depending on the experiment, although the flow rate had no influence on the reaction product and

TABLE 1: Reaction Products and Conversion Yields of NO in Ar/NO/ O_2 Mixtures

reaction mixture	NO decomposition (%)	reaction products
Ar/NO	88 ^a	N_2, O_2
Ar/NO/ O_2	65–81 ^b	N_2, O_2

^a Data are reported for a total pressure of 45 Torr. For other pressures differences of up to 10% have been found. ^b Interval of conversion as a function of pressure.

efficiency. The total pressure in the reactor was controlled by adjusting a throttle valve placed between the reactor and a vacuum pump. Experiments were carried out for different compositions of the gas mixtures around the aforementioned values and total pressures between 30 and 75 Torr. Analysis of the gas mixtures before and after plasma ignition is done by a quadrupole mass spectrometer (QMS422 from Balzers). The gas mixtures are sampled to the mass spectrometer through a calibrated leak valve. Calibration of the peak intensities is carried out with simple mixtures of Ar with either the reactants or the gases obtained as products of the reactions. The accuracy of the analysis is considered to be within 10% of maximum uncertainty. The induction period to reach steady-state conditions was very small, in any case shorter than 10 s.

Study of the plasma by OES is carried out by collecting the light with an optical fiber and analyzing the emitted spectra with a scanning monochromator. The whole system was operated and the signals collected with a personal computer.

III. Results

A. Mixtures Ar/NO/ O_2 . The detected products after plasma excitation of this gas mixture were O_2 and N_2 . No traces of NO_2 or any other nitrogen oxides were detected for the different concentrations of O_2 studied. A percentage of 88% decomposition was found for mixtures Ar/NO without O_2 (cf., Table 1). The influence of the O_2 concentration on the reaction yield is reported in Figure 2. Figure 2a shows the percentage of decomposition of NO for different concentrations of O_2 in the gas mixture as a function of the total pressure in the reactor. As a general effect, this figure shows that, within the pressure range studied, the total pressure has little effect on the reaction yield. This situation was also found for the other gas mixtures studied in this work and, therefore, this parameter will not be considered explicitly in the next sections. According to this figure, when there is no O_2 in the gas mixture, NO decomposes into N_2 and O_2 from a minimum of 80% at 30 Torr to a maximum of 90% at 75 Torr. The decomposition yield decreases as the amount of O_2 in the mixture changes from 0% to 5%. For this latter situation, the NO decomposition varies from 57% at 30 Torr to 65% at 75 Torr. This evolution with the addition of O_2 suggests that the simultaneous presence of N_2 and O_2 in the plasma mixture leads to a series of intermediate reactions that end up with the formation of NO and, therefore, decrease the overall yield of NO removal. To check this possibility, a mixture of 1% N_2 and 3% O_2 was studied under similar working conditions. This experiment yields the formation of NO (about 150–175 ppm), thus confirming that nitrogen atoms generated through the decomposition of NO may intervene in a side reaction with O_2 to generate NO_2 .^{2,12,16} To check the influence of this process under our working conditions, we have followed the percentage of decomposition of NO (3000 ppm) in a mixture Ar (carrier gas) + O_2 (3%) and different concentrations of N_2 . The results of this experiment are reported in Figure 2b, showing that the addition of 1% N_2 to the reaction mixture decreases the efficiency of the decomposition of NO by about 10% for

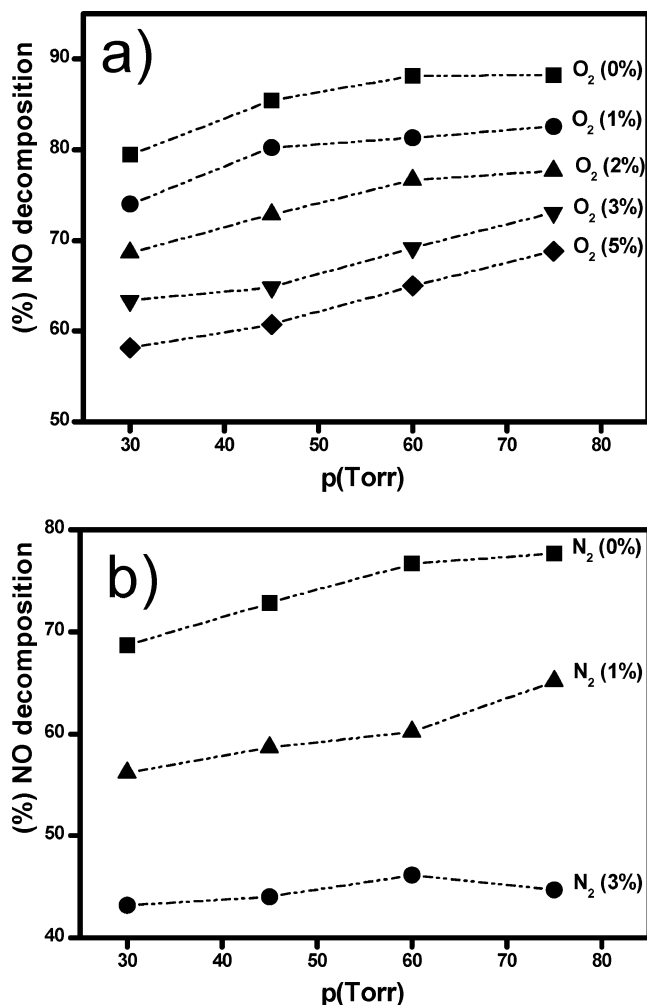


Figure 2. (a) Percentage of decomposition of NO for different concentrations of O₂ in the gas mixture as a function of the total pressure in the reactor. (b) Percentage of decomposition of NO for different concentrations of N₂. The amount of NO is 3000 ppm.

the whole pressure range, and by ca. 15–20% when the concentration of N₂ is 3%. However, we would like to indicate that this tendency has to be associated with the high concentration of Ar in the gas mixture. In fact, in experiments similar to those reported here but with N₂ as carrier gas, the extent of NO decomposition reached values similar to those found here for mixtures Ar/NO.³⁵

It is interesting to mention that for the present series of experiments the total flow of Ar was kept between 25 and 50 sccm and that the actual value of this parameter had practically no influence on the reaction yield. This means that, within the studied flow ranges, the residence time of the gases in the plasma zone has no influence on the final result.

The analysis by OES of the plasma intermediates reveals the presence of NO*, N₂* and different species of excited oxygen. Typical spectra corresponding to NO* and N₂* species are shown in Figure 3, together with a peak attributed to OH* groups. This latter species must be formed by reaction of the excited forms of oxygen with some residual hydrogen and/or directly generated by dissociation of water initially adsorbed in the reactor walls. When O₂ was added to the reaction mixture, Figure 3 shows that the relative intensity of NO* bands increases, thus supporting the participation of oxygen in the reaction channels leading to the formation of NO by direct reaction with nitrogen atoms.^{2,16} In Table 2 we report a summary of the position of the main emission peaks for all reaction

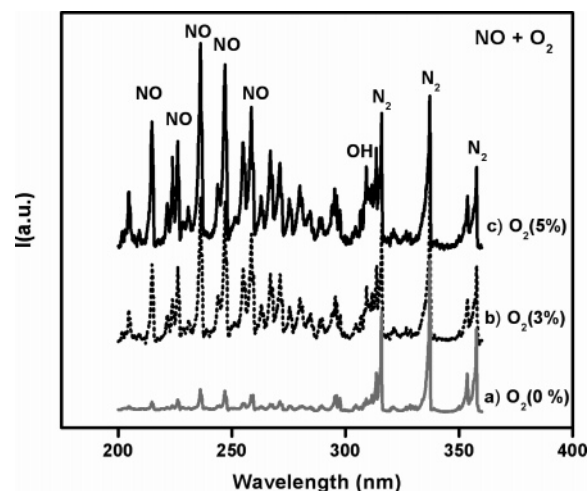


Figure 3. Optical emission spectrum taken from a plasma of the gas mixture Ar/NO/O₂ for different concentrations of O₂: (a) Ar/NO; (b) Ar/NO/O₂(3%); (c) Ar/NO/O₂(5%).

mixtures and their attribution to different species according to previous literature assignments.^{36–38}

B. Mixtures Ar/NO/CH₄. The analysis of the plasma reaction of the Ar/NO/CH₄ mixture pretends to discern the effect of the hydrocarbons on the plasma decomposition mechanism of NO. To account for this process, we report first the decomposition reaction of CH₄ in a mixture Ar/CH₄. We found that CH₄ decomposes practically totally to yield H₂ and traces of C₂ hydrocarbons. The conversion degree of CH₄ into H₂ amounted to ca. 90%. Another majority reaction product was carbon, which appeared as a deposit on the inner walls of the reaction tube in the zone of the plasma discharge around the surfatron (cf. Figure 1). The formation of carbon deposits interfered with the decomposition reaction because it absorbed the microwave power, became very hot (the carbon deposits became red), and extinguished the plasma. Owing to these circumstances no systematic characterization of the plasma was possible by OES.

For the Ar/NO/CH₄ mixture the amount of deposited carbon was smaller and the OES analysis of the plasma could be carried out systematically. For this mixture, the main reaction products were N₂, H₂O, CO, C₂ hydrocarbons (C₂H₄ and/or C₂H₂) and H₂, plus carbon in the form of a deposit. A minority product produced during this reaction was HCN (cf. Table 3). The percentage of removal of NO was higher than 95% and N₂ was the main nitrogen containing product, although traces of HCN were also formed (i.e., appearance of a MS peak of mass 27, typical of CN species). Figure 4a shows an OES spectrum of the plasma for the Ar/NO/CH₄ mixture without oxygen. It is characterized by peaks due to CN* species, CH* species and the Swan system of C₂* species.^{36–38} Small peaks due to OH* and H* species can be also seen in this spectrum. Table 2 summarizes the peak position and other spectral characteristics of the intermediate species detected for this mixture under our working conditions. C₂* species can be considered as intermediate species previous to the formation of carbon deposits.³⁸ The unequivocal presence of emission peaks due to CN* confirms the formation of HCN as a byproduct of the plasma reaction between NO and CH₄. Owing to the noxious character of HCN, its eventual formation during plasma decomposition processes involving NO and hydrocarbons is of much concern and has to be carefully investigated. In this respect, it must be mentioned that its formation in other NO technologies is by no means zero^{39–41} and sometimes is also detected during catalytic abatement of NO.⁴²

TABLE 2: Summary and Attribution of the Main Bands and Peaks Detected by OES for the Different Gas Mixtures

reaction mixture	species (system)	electronic transition	peak position/interval range
Ar/NO/O ₂	N ₂ (second positive)	C ³ Π → B ³ Π	281.43–497.64
	NO (γ system)	A ² Σ ⁺ → ² Π	195.61–345.85
Ar/NO/CH ₄	OH (3064 system)	² Σ → ² Π	260.85–347.21
	CN (violet system)	² Σ → ² Σ	358.59–460.61
	CH (4300 system)	³ Π → ³ Π	431.25–494.0
	C ₂ (Swan system)	³ Π → ³ Π	436.52–667.73
	CO (third positive and 5B)	b ³ Σ → a ³ Π	283.31–382.51
Ar/CH ₄ /O ₂ (3%)	OH (3064 system)	² Σ → ² Π	260.85–347.21
	H	² p ⁰ → ² D	656.28; 486.13; 434.05
	O	³ S ⁰ → ³ P	777.19; 777.42; 844.64
	CH (4300 system)	³ Π → ³ Π	431.25–494.0
	CO (third positive and 5B)	b ³ Σ → a ³ Π	283.31–382.51
	C ₂ (Swan system)		
Ar/CH ₄ /O ₂ (0.3%)	H	³ Π → ³ Π	436.52–667.73
	CH (4300 system)	² p ⁰ → ² D	656.28; 486.13; 434.05
Ar/NO/CH ₄ /O ₂ (3%)	OH (3064 A system)	³ Π → ³ Π	431.25–494.0
	H	² Σ → ² Π	260.85–347.21
	CN (violet system)	² p ⁰ → ² D	656.28; 486.13; 434.05
	CO (third positive and 5B)	² Σ → ² Σ	358.59–460.61
	CH (4300 system)	b ³ Σ → a ³ Π	283.31–382.51
	N ₂ (second positive)	³ Π → ³ Π	431.25–494.0
Ar/NO/(C) ^a	C ³ Π → B ³ Π	C ³ Π → B ³ Π	281.43–497.64
	CN (violet system)	² Σ → ² Σ	358.59–460.61
	C ₂ (Swan system)	³ Π → ³ Π	436.52–667.73

TABLE 3: Reaction Products and Conversion Yields of NO in Ar/NO/CH₄ Mixtures (Effect of the Hydrocarbons)

reaction mixture	NO decomposition (%) ^a	CH ₄ decomposition (%) ^a	reaction products ^b
Ar/NO/CH ₄ (0.15%)	98	94	N ₂ , CO (700), H ₂ O (2300), H ₂ ^d (300), HCN (traces), C _x H _y (200), C ^c
Ar/NO/CH ₄ (0.3%)	96	94	N ₂ , CO (1500), H ₂ O (1500), H ₂ ^d (3300), HCN (traces), C ₂ H _y (600), C ^c
Ar/NO/CH ₄ (0.5%)	97	96	N ₂ , CO (2000), H ₂ O (1000), H ₂ ^d (6000), HCN (traces), C _x H _y (1500), C ^c

^a Data are reported for a total pressure of 45 Torr. For other pressures differences of up to 10% have been found (the amount of NO is 3000 ppm). ^b In parentheses are reported estimated concentrations in ppm. These figures are affected by an estimated error of 10–20%. ^c Deposits of solid carbon detected by visual inspection. ^d The amount of hydrogen has been estimated as a difference from the initial amount of this element present in CH₄ and that in the reaction products containing it (e.g., H₂O and C₂H₄/C₂H₂ hydrocarbons). For the calculations it is assumed that the hydrocarbons are C₂H₄.

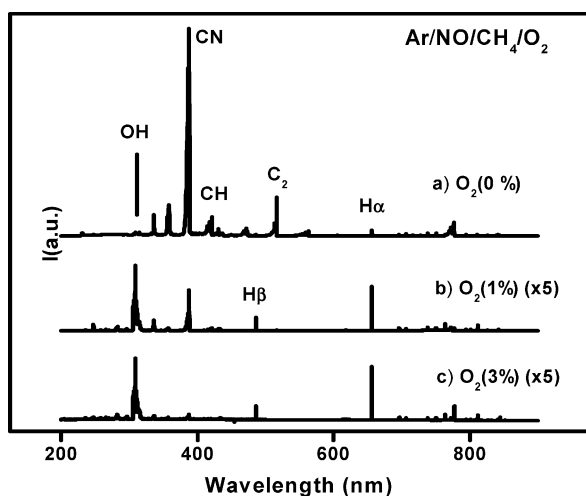


Figure 4. Optical emission spectra taken from a plasma of the gas mixtures Ar/NO/CH₄ (a), Ar/NO/CH₄/O₂(1%) (b), and Ar/NO/CH₄/O₂(3%) (c).

C. Mixtures Ar/CH₄/O₂. Before reporting the results of a quaternary mixture of NO plus oxygen and the hydrocarbon, it is convenient to comment about the results with CH₄ and O₂ as the sole diluted components and 5000 ppm of CH₄. Several experiments were carried out with mixtures containing different concentrations of O₂ from 0.3 to 3%. Main products of the plasma reaction were CO, H₂O, and H₂ for O₂ concentrations higher than 1%. For a concentration smaller than this value,

carbon deposits and C₂ hydrocarbons (C₂H₂ and/or C₂H₄) were formed. Small amounts of CO₂ were also detected in all cases. A summary of the different reaction products and their relative concentrations is reported in Table 4. The obtained results clearly indicate that methane is burned with an excess of oxygen. By contrast, for low O₂ concentrations, plasma reaction of CH₄ proceeds through the partial heterolytic decomposition of the hydrocarbons into C and H₂ and the formation of minority amounts of C₂ or higher hydrocarbons (mainly C₂H₄ and/or C₂H₂). Re-forming of methane into H₂ using plasmas is a process of large industrial interest, by which the formation of higher hydrocarbons as byproducts of the reaction occurs to a different extent depending on the type of plasma and other experimental parameters.^{42–47}

Figure 5 shows two spectra for reaction mixtures rich and poor in oxygen. The most significant difference between the two situations is the enhancement of the intensity of the bands of the Swan system of C₂* species for the mixture with little oxygen, thus coinciding with the formation of carbon deposits as a main reaction product. We attribute the formation of these species to the first steps in the condensation reactions leading to the formation of carbon deposits. In contrast, for oxygen rich conditions, C₂* bands disappeared, whereas the relative intensity of the peak due to OH* radicals greatly increases (cf. Table 2). Also, the spectrum reveals the development of intense peaks due to the Balmer series of atomic hydrogen and some peaks due to atomic oxygen. CH* species can be also detected under these conditions.

TABLE 4: Reaction Products in Ar/CH₄/O₂ Mixtures Containing Different Concentrations of O₂

reaction mixture	CH ₄ decomposition (%) ^a	reaction products ^b
Ar/CH ₄ /O ₂ (3%)	99	CO (2300), CO ₂ (300), H ₂ O (2200), H ₂ (3800) ^d
Ar/CH ₄ /O ₂ (1%)	99	CO (2200), CO ₂ (300), H ₂ O (5000), H ₂ (1000), ^d C ^c
Ar/CH ₄ /O ₂ (0.6%)	99	CO (2000), CO ₂ (100), H ₂ O (4000), H ₂ (2000), ^d C ^c
Ar/CH ₄ /O ₂ (0.3%)	93	CO (1300), H ₂ O (700), H ₂ (3300), ^d C _x H _y (1000), C ^c

^a Data are reported for a total pressure of 45 Torr. For other pressures differences of up to 10% have been found. ^b In parentheses are reported estimated concentrations. These figures are affected by an estimated error of 10–20%. ^c Deposits of solid carbon detected by visual inspection. ^d The amount of hydrogen has been estimated as a difference from the initial amount of this element present in CH₄ and that in the reaction products containing it (e.g., H₂O and C₂H₄/C₂H₂ hydrocarbons). For the calculations it is assumed that the hydrocarbons are C₂H₄.

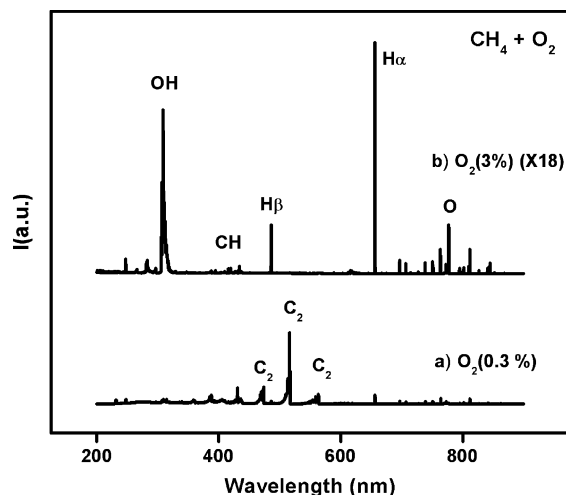


Figure 5. Optical emission spectra taken for a plasma of the gas mixtures Ar/CH₄/O₂(0.3%) (a) and Ar/CH₄/O₂(3%) (b).

D. Mixtures Ar/NO/CH₄/O₂. The composition of this quaternary mixture resembles that of some real gas exhausts produced by combustion engines (the absence of H₂O and CO₂ is an important difference, although they are formed as products of the plasma reaction).^{6,9,14,21,22,29} Two different experiments have been carried out by fixing the O₂ concentrations at 1% and 3%, respectively. In the former case, a carbon deposit was formed during the plasma reaction. By contrast, for 3% O₂, no carbon was formed. The main reaction products under the two conditions were N₂, CO, H₂O, and H₂, accompanied by some small amounts of CO₂ as the minority component (cf. Table 5). It is interesting that in the presence of O₂, no traces of HCN could be detected as reaction product. This result contrasts with the aforementioned formation of this molecule by plasma activation of mixtures Ar/NO/CH₄. However, the OES observation of the reaction intermediates (cf., Figure 4b,c) still reveals the appearance of bands due to CN* species, although with a relative intensity smaller than that of these species in the mixture without oxygen (cf. Figure 4a). In addition to the peaks corresponding to this species, bands due to OH* radicals, CH* species and the peaks of the Balmer series of hydrogen are also observed in the spectrum.

E. Reaction of Ar/NO Plasmas with Carbon. The formation of carbon by plasma decomposition of CH₄ is sometimes reported during plasma re-forming of this hydrocarbon to produce H₂ and/or higher hydrocarbons.^{42–47} Formation of carbon deposits has also been found here for mixtures poor in O₂. Carbon can be considered as a chemical with reductive character and its presence as soot particles in diesel exhausts justifies an investigation to check whether NO containing plasmas react directly with solid carbon. In this line of thinking we have carried out an experiment where an Ar/NO plasma interacts with a carbon deposit located downstream from the surfatron position. Mass spectrometric analysis of the gas mixture shows that, as a result of the carbon–plasma interaction,

N₂, O₂, and CO form as main reaction products, whereas the carbon deposit is progressively burned off. The percentage of NO decomposition amounts to a value higher than 96% for the whole range of gas pressures studied. The virtual total decomposition of NO under these conditions contrasts with the 80–88% removal found for mixtures Ar/NO without O₂ (cf. Figure 1a and Table 1). This is also the percentage found when no carbon remains in the reactor tube, once it is burned off by the plasma.

During this experiment, three different colored zones are observed around the carbon deposits. The optical emission spectra of these three zones are different, as illustrated in Figure 6. The spectra in the zone up from the carbon deposit area are very similar to that of the NO/Ar plasma reported in Figure 3; i.e., it is representative of the dissociative processes of NO presented in a previous section. The spectrum completely changes when one looks at the two other zones. In the carbon zone the spectrum depicts very intense bands due to CN* species and excited N₂* species and some of the Swan bands due to C₂* species. This spectrum confirms that the CN* species forms as an intermediate of the reaction of nitrogen oxide with carbon. On the other hand, the detection of bands due to the C₂* species proves that these are intermediate species of both the formation of solid carbon (i.e., see Figure 5a) and its removal by reaction with an Ar/NO plasma. The spectrum slightly changes in the zone down from the location of the carbon deposits. Here, the C₂* bands disappear, whereas the intensity of CN* bands decreases and that of N₂* species increases. This indicates that decomposition of NO into N₂ is approaching its completion.

IV. Discussion

A. Ar/NO and Ar/NO/O₂ Mixtures. NO decomposition in plasmas of simple gas mixtures have been widely studied in the literature. Typical mixtures consist of NO with O₂,^{12,13,16,19,25–27} and eventually water vapor.^{19,20,48} Ar or other noble gases are typical carrier gases for these studies. Different types of plasma excitations have been used for this type of study, including atmospheric pressure pulsed microwave discharges (PMW),^{25–28,45,46} corona and dielectric barrier discharges (DBD),^{2,8,9,11,12,15,16,18,19,29} or hollow cathode discharges.²³ In all cases, removal of NO is reported although the reaction pattern differs from PMW discharges to corona or DBD. For PMW most studies report dissociation of NO into N₂ and O₂, whereby the addition of O₂ and/or H₂O produces a decrease in the decomposition yield. By contrast, several works dealing with DBD report that the presence of O₂ and NO in the reaction mixture leads to the formation of NO₂.^{2,12,14,15,16,18} This process is proposed as the basis of procedures consisting of a first oxidation step of NO into NO₂ and a second catalytic stage involving a conventional reduction step of NO₂ into N₂.^{6,12,14–16,21,22,47} Kinetic models and spectroscopic studies of the plasma chemistry of these simple gas mixtures have permitted us to formulate precise descriptions of the intermediate reactions leading to the final products.

TABLE 5: Reaction Products and Conversion Yields of NO and CH₄ in Ar/NO/CH₄/O₂ Mixtures

reaction mixture	NO decomposition (%) ^a	CH ₄ decomposition (%) ^a	reaction products ^b
Ar/NO/CH ₄ (0.3%)/O ₂ (1%)	97	99	N ₂ , CO (2100), CO ₂ (400), H ₂ O (5900), C ^c
Ar/NO/CH ₄ (0.3%)/O ₂ (3%)	87	99	N ₂ , CO (2200), CO ₂ (400), H ₂ O (2300), H ₂ ^d (3700)
Ar/NO/CH ₄ (0.5%)/O ₂ (1%)	93	99	N ₂ , CO (2200), CO ₂ (400), H ₂ O (8400), H ₂ ^d (2100)
Ar/NO/CH ₄ (0.5%)/O ₂ (3%)	90	99	N ₂ , CO (2100), CO ₂ (400), H ₂ O (8000), H ₂ ^d (2000)

^a Data are reported for a total pressure of 45 Torr. For other pressures differences of up to 10% have been found. ^b In parentheses are reported estimated concentrations. These figures are affected by an estimated error of 10–20%. ^c Deposits of solid carbon detected by visual inspection. ^d The amount of hydrogen has been estimated as a difference from the initial amount of this element present in CH₄ and that in the reaction products containing it (e.g., H₂O and C₂H₄/C₂H₂ hydrocarbons). For the calculations it is assumed that the hydrocarbons are C₂H₄.

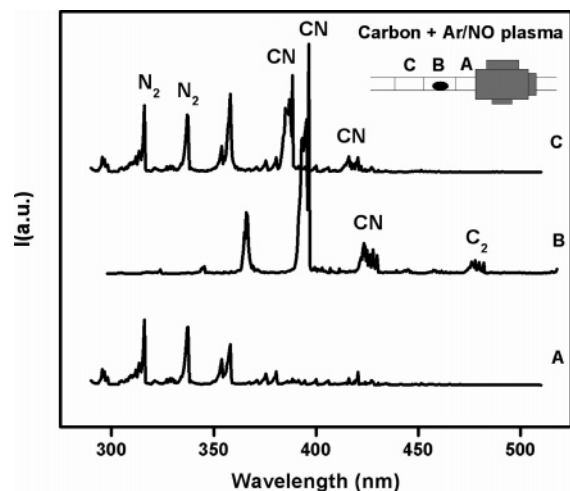
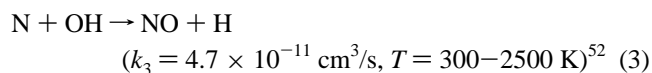
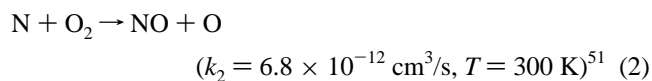
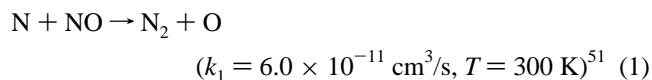


Figure 6. Optical emission spectra taken for the reaction of an Ar/NO plasma with carbon deposits. (A) Zone previous to the location of the carbon deposits. (B) Zone of carbon deposits. (C) Zone afterward the location of the carbon deposits. For clarity, spectrum B has been shifted to the right.

Our results with the microwave SW reactor are similar to those reported for PMW discharges because in the two cases the major reaction products of the plasma decomposition of NO are N₂ and O₂. Electrons initially interacting with NO and/or N₂ or O₂ molecules are the initiating species for the overall reaction chain.^{18,20,28,49} The use of Ar as carrier gas contributes to the generation of these free electrons due to the well-known tendency of this gas to ionize under plasma conditions.³⁹ The observation that the NO SW removal efficiency decreases as the amount of O₂ in the reactant flow increases is also in agreement with these previous PMW studies.^{26–28} According to literature⁵⁰ the three following elemental reactions can be important for both the decomposition of NO and its formation in an oxygen rich flow:



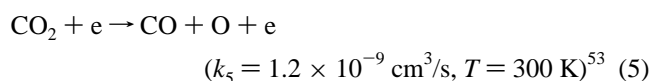
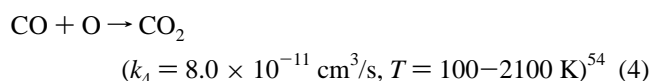
In the three reactions, the N atoms play an important role, either for the NO removal via eq 1 or for its production by reaction with O₂ or OH (cf. eq 2 and 3).

B. Ar/CH₄ and Ar/CH₄/O₂ Mixtures. In contrast to the numerous theoretical and experimental studies dealing with the plasma reaction of NO in simple mixtures of this molecule with O₂,^{19,25–27} N₂,^{26–28} CO₂⁵³ or H₂O,^{19,20,48} the analysis of the

processes occurring for more complex mixtures has been generally less addressed in the literature. The results reported here constitute an empirical evaluation of the overall processes taking place in complex gas mixtures. SW plasma activation of an Ar/CH₄ mixture produces the re-forming of the methane with formation of solid carbon and H₂ as majority products. The formation of C₂ or higher hydrocarbons such as C₂H₂ and/or C₂H₄ by using methane as main reactant has been extensively studied and reported,^{41,42–46} but it is a secondary process under our experimental conditions. Thus, Heintze et al.,⁴² with a PMW system and mixtures CH₄ (88%) and Ar (12%), only report the formation of C₂ hydrocarbons (ethane, ethene, or acetylene depending on experimental parameters). Very likely, the much lower concentration of CH₄ in our reaction mixture is the reason for the observed difference.

In our experiment we have found that the addition of O₂ to the reaction mixture prevents the formation of carbon deposits. According to Table 4, this finding is consistent with the fact that the direct dissociation of CH₄ into C and H₂ is replaced by reaction processes yielding H₂ plus CO or H₂O + CO as final products according to the overall equations: CH₄ + 1/2 O₂ → 2H₂ + CO, and CH₄ + 1/2 O₂ → 2H₂O + CO (note that these equations do not mean single reaction steps, but a stoichiometric balance of atoms between initial reactants and final products).

Only for higher concentrations of O₂ in the reaction mixture does the production of CO₂ start to be significant. The following elemental reactions involving CO and CO₂ can be invoked to explain this finding⁵⁰



According to reaction 4, an increase in the concentration of oxygen may contribute to the formation of CO₂, although it is not rare that this product always forms in small concentrations owing to the high rate constant of reaction 5 involving its direct dissociation by electron impact.^{14,38}

The spectra recorded for mixtures Ar/CH₄/O₂ are characterized by peaks due to CO*, OH*, H*, and O* radicals. They must be some of the intermediate species intervening in the overall reaction processes with CH₄ and CO₂. These radicals must be formed by collision of electrons with CH₄ (i.e., H* and CH*), CO₂, and oxygen molecules (i.e., O*) and by secondary reactions between them (i.e., CO* and OH*). Reactions involving these radicals and their rate constants have been previously reported.^{37,44–47} In our experiment, it is interesting to stress that with oxygen rich mixtures no C₂* and very little CH* radicals were detected. The opposite situation occurs with mixtures poor in oxygen, for which C₂* and CH* species give rise to the most intense bands in the spectrum (cf. Figure

5). This suggests that C_2^* radicals are precursor species in the formation of carbon deposits according to an overall process of the type, $CH_4 \rightarrow C(s) + 2H_2$ (note that this is a heterogeneous process involving the formation of a solid phase).

In the paper by Heintze et al.,⁴² describing the formation of C_2 hydrocarbons from methane, C_2^* species together with CH^* and H^* were also detected by OES, although formation of solid carbon was not reported. Very likely, the high concentration of H^* radicals existing under the working conditions of these authors (i.e., mixtures 82% CH_4 , 18% Ar) prevents the direct dissociation and favor the formation of C_2 hydrocarbons. This will be in agreement with the well-known efficiency of hydrogen radicals to react directly with carbon⁵⁵ and/or with a plasma reaction such as



C. Ar/NO/ CH_4 Mixtures. From a chemical point of view, though NO and O_2 are molecules with oxidative character, H_2 , CH_4 , or other hydrocarbons are reductive. It is therefore likely that plasma activation of Ar/NO/ CH_4 mixtures may lead to the reduction of NO molecules. It has been reported that hydrocarbons such as C_2H_4 ,^{10,11} C_3H_6 ,^{9,46} and C_3H_8 ⁴⁶ are rather effective for NO and NO_2 reduction to molecular nitrogen, whereas methane is less effective for this process.⁴⁶ Kushner and co-workers^{9,56,57} have studied experimentally and theoretically the DBD plasma reaction of NO_x mixtures (i.e., NO + NO_2) and hydrocarbons. They found that the amount of hydrocarbon, although affecting positively the NO decomposition, does not alter the overall NO_x conversion (i.e., the sum of NO + NO_2). Other authors have studied the plasma reaction between NH_3 and NO, showing that the addition of ammonia (i.e., another molecule with reductive character used in conventional catalytic processes for the abatement of NO_x in big combustion plants⁵⁸) improves the removal efficiency of NO_x .²¹ In our experiment, practically 100% removal of NO is achieved with Ar/NO/ CH_4 mixtures. This removal may occur through the following two overall processes that imply the oxidation of CH_4 with NO: $CH_4 + NO \rightarrow CO + \frac{1}{2}N_2 + 2H_2$ and/or $CH_4 + 2NO \rightarrow C + 2H_2O + N_2$ (note again that these two equations do not refer to actual elemental plasma reactions but to the atomic stoichiometric balance between reactant and products).

We must stress that the lack of NO_2 formation with the SW reactor under our working conditions contrasts with the hydrocarbon enhancement of the yield toward this molecule in DBD.^{8,11} Very likely, the relatively high specific input energy used in our case can be a factor contributing to the observed difference.

Besides N_2 , CO, solid C, H_2 , and H_2O , which are the major products of the SW plasma reaction of this mixture, other products such as C_2H_2 and/or C_2H_4 hydrocarbons and minority components such as HCN are also formed. Owing to the very noxious character of this latter molecule, its eventual formation during any NO plasma abatement process is of the greatest concern.

Plasmas of mixtures of NO with CH_4 have recently received much attention in connection with the formation of C deposits on the walls of fusion reactors.⁵⁹ The addition of NO to the gas mixture has been proposed as an efficient scavenger to quench the formation of H^* radicals responsible for the generation of the deposits. In these studies, the formation of some HCN as reaction product and the evolution of very intense emission lines due to CN^* have been also reported.⁶⁰ The OE spectra recorded here also show the development of very intense peaks due to CN^* radicals (cf. Figure 4a) and small bands of the Swan series

due to C_2^* species, whose formation has been related to the production of carbon deposits. It is likely that a mechanism similar to that discussed in the context of cold fusion reactors to prevent the formation of carbon is responsible here for the formation of CN^* intermediate radicals and HCN as a final product.

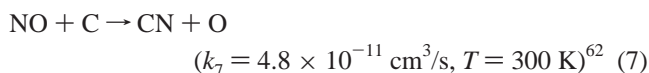
D. Ar/NO/ CH_4 / O_2 Mixtures. In heterogeneous catalytic reactions intended for the removal of NO in oxygen rich streams, a critical problem is to achieve the selective reduction of NO in the presence of oxygen. A similar objective should be fulfilled by plasma removal of NO. In this respect the present results with the quaternary mixture Ar/NO/ CH_4 / O_2 in the SW reactor are very promising. Major products of this process are N_2 , CO, and H_2O , whereas a carbon deposit also forms in streams poor in oxygen. CO_2 appears as a minor product. Also, it must be remarked that no HCN is detected as the final product of the reaction. Thus, the overall process can be considered as resulting from the direct oxidation of CH_4 by NO (see previous section), the conversion of CH_4 into solid carbon depending on the oxygen concentration and the oxidation of CH_4 with O_2 . Moreover, direct dissociation channels of NO into N_2 and O_2 must not be discarded (cf. eqs 1 and 2). Overall, practically 100% removal of NO is obtained.

The hypothesis that the plasma behavior of Ar/NO/ CH_4 / O_2 mixtures can be considered as the superposition of the processes involved with ternary mixtures Ar/NO/ CH_4 and Ar/ CH_4 / O_2 without significant interferences between them is further supported by the OES spectra recorded for the quaternary mixture. In fact, the spectrum in Figure 4b can be considered as the superposition of the spectra shown in Figures 4a and 5b, corresponding to the ternary mixtures. It is also interesting that, despite the formation of intermediate CN^* radicals deduced from the OE spectrum of the quaternary mixture, no HCN is formed as reaction product. Very likely, the CN^* radicals are destroyed by the O_2 present in the gas flow and/or by intermediate active species of oxygen, thus preventing the formation of HCN as a stable final product.

Another interesting result from Table 5 is that CH_4 is completely burned off in the quaternary mixture. This means that in the SW reactor both the decomposition of NO and the removal of CH_4 are achieved in a single process.

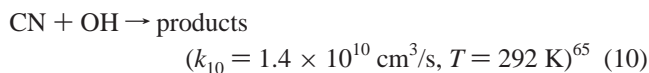
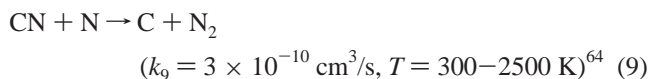
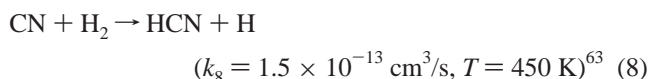
E. Reaction of NO/Ar Plasmas with Solid Carbon. To our knowledge, few studies have previously addressed the plasma removal of NO in the presence of soot particles in the gas streams.^{6,14,29,30} Chae et al.⁶ worked with a DBD reactor connected to a diesel engine and found that NO_2 formed in the plasma device was able to react directly with the soot particles. Kushner et al. also postulated a surface reaction between NO_2 chemisorbed and the carbonaceous surface of soot particles.^{9,29} Our experiment consisting of the direct exposure of a carbon deposit to an Ar/NO plasma clearly evidences that solid carbon is active for the removal of NO. Although further studies are still necessary to get a clear picture of this heterogeneous plasma–solid reaction, the analysis of the products and the peaks appearing in the recorded spectra provides some hints to understand this complex process. N_2 , O_2 , and CO are detected as main products, indicating that part of the oxygen produced by the dissociation of NO reacts with the carbon. The overall reaction of this process is $NO + C_{sol} \rightarrow CO + N$. Although the experimental conditions are completely different from the plasma/solid reaction meant by the previous equation, it is interesting that a similar reaction (i.e., $NO + C \rightarrow CO + N$)⁶¹ is also feasible between plasma species with a rate constant of $k = 3.49 \times 10^{-11} \text{ cm}^3/\text{s}$ at $T = 300 \text{ K}$.

However, as suggested by the spectra in Figure 6, the reaction mechanism of the plasma/solid carbon must be rather complex. In fact, the spectra in this figure can be considered as the superposition of the spectra corresponding to the plasma dissociation of NO (cf. Figure 3) and the bands of the CN* and C₂* radicals. A plasma reaction that would be able to yield CN under our working conditions is⁵⁰



Because signals due to CN* and C₂* species are predominant in the zone of the reactor with deposited carbon, its formation suggests that not only oxygen radicals but also N* radicals may react directly with the solid carbon, leading to the formation of intermediate CN* radicals. The fact that, within the sensitivity limit of our system, no HCN is detected has to be attributed to the lack of hydrogen under these conditions.

The complexity of the reaction process is further supported by the detection of C₂* only in the zone with C deposits. The formation of these species might be accounted for by either plasma reactions between radicals such as⁹



or the etching of the solid carbon by the activated species of the Ar plasma (e.g., electrons, several radicals, etc., CN* and C₂*). Taking into account the rate constant and temperatures of reactions 8 and 9, we are inclined to assume that a heterogeneous etching process is primarily responsible for the formation of the different species. In fact, etching of carbon surfaces by a plasma of Ar is a very well-known phenomenon that has been used to create different types of defects on the surface of graphite.⁶⁶

V. Concluding Remarks

SW reactors have been successfully used for the removal of volatile organic compounds (VOCs) at room temperature.^{31–33} The previous results and discussion have shown that this type of plasma reactor can be successfully used for the removal of NO in complex exhausts. The small size of this type of MW devices and the fact that they can be operated with cables (i.e., they do not require the big waveguide applicators typically used in conventional MW and PMW reactors^{24–28}) are clear advantages that support its practical implementation. However, because Ar is used as carrier gas, the results reported in this work should be still considered as preliminary. In diesel or other combustion exhausts the main component is N₂, a molecule that may contribute to the formation of NO by plasma reaction with O₂. Therefore, a careful study of the plasma processes occurring with mixtures similar to those considered here, but with N₂ as carrier gas seems indispensable to prove the suitability of SW plasma reactors to remove NO under real conditions. The influence of other components present in real outlets such as H₂O or CO₂ should be also considered, because previous works in the literature^{19,20,48,53} with simple mixtures of NO and these

gases suggest that these molecules, similarly to O₂, tend to decrease the dissociation yield of NO into N₂ and O₂. In this regard, our results have shown that oxygen is critical for the control of the overall reaction processes and demonstrate that its presence in the plasma, though in relatively low concentration, may modify significantly the plasma chemistry of complex mixtures. Thus, for example, we have shown that oxygen prevents the formation of carbon deposits from dissociation of methane. Oxygen also prevents the formation of HCN in mixtures of NO/CH₄. These effects are very important for a safe use of plasmas in actual devices and should be taken into account for their practical implementation.

A final remark concerns the specific input energy density used in our experiment. The used energy is relatively high in our case because it favors the dissociation of NO. Work is being carried out in our laboratory to check systematically the influence of such a parameter in the NO removal efficiency with a SW device.

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