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# Phenol Production in Benzene/Air Plasmas at Atmospheric Pressure. Role of Radical and Ionic Routes

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Benzene can be efficiently converted into phenol when it is treated by either corona or dielectric barrier discharge (DBD) plasmas operating at atmospheric pressure in air or mixtures of $N_2$ and $O_2$. Phenol produced by corona discharge in an atmospheric pressure chemical ionization source (APCI) has been detected as the corresponding radical cation $C_6H_5OH^{+\bullet}$ at *m*/*z* 94 by an ion trap mass spectrometer. On the other hand, phenol has been observed also as neutral product by gas chromatography−mass spectrometry analysis (GC−MS) after treatment in a DBD plasma. Experiments aimed at shading light on the elementary processes responsible for benzene oxidation were carried out (i) by changing the composition of the gas in the corona discharge source; (ii) by using isotopically labeled reagents; and (iii) by investigating some relevant ion−molecule reactions (i.e. $C_6H_6^{+\bullet} + O_2$, $C_6H_5^{+} + O_2$) via selected guided ion beam measurements and with the help of *ab initio* calculations. The results of our approach show that ionic mechanisms do not play a significant role in phenol production, which can be better explained by radical reactions resulting in oxygen addition to the benzene ring followed by 1,2 H transfer.

## 1. Introduction

The synthesis of phenol is an important process in the chemical industry, due to the increasing applications of phenol for the production of resins, fibers, anesthetics, and disinfectants. Phenol is commonly produced from benzene and propylene in the three-step cumene synthesis; however, this process has several drawbacks due to environmental and energetic problems. For this reason, interest in the one-step hydroxylation of benzene leading to phenol is continuously growing. Beside well-established research on the development of suitable catalysts,[1] it has been demonstrated recently that phenol can be produced also in nonthermal plasma systems,[2−5] which are characterized by different temperatures of electrons, ions, and neutral species. Such plasmas are efficient sources of highly reactive species which can redirect the applied electric energy into chemical energy and promote energetically disfavored chemical processes.

We have observed the production of phenol cations $C_6H_5$-$OH^{+\bullet}$ (*m*/*z* 94) when a sustained flow of benzene is injected into the corona discharge of an atmospheric pressure chemical ionization source coupled with an ion trap mass spectrometer (APCI−MS). Such a source is very selective toward stable ions because chemical equilibrium conditions are usually achieved,[6,7] leading mainly to the formation of protonated molecular ions.[8,9] Even if it is widely accepted that APCI is a soft ionization technique, it has been recently shown that it may act as a true chemical reactor.[10,11]

The formation of neutral phenol has been observed also when a mixture of benzene, nitrogen, and oxygen is treated in a dielectric barrier discharge (DBD) at atmospheric pressure connected to a GC−MS (gas chromatograph mass spectrometer) analyzer. Dielectric barrier discharges are characterized by a relatively high electron energy (4−8 eV) and low gas temperature (300−400 K). The combination of these properties makes DBDs efficient in promoting gas phase chemistry and polymerization.[12]

The concurrent detection of ionic and neutral products obtained from benzene oxidation in plasma systems has prompted an investigation on some aspects of the hydroxylation of benzene into phenol. Hereafter the conceivable ion chemistry producing phenol has been reviewed and the most relevant ion−molecule reactions have been studied experimentally by a guided ion beam tandem mass spectrometer (GIB-MS), and theoretically through *ab initio* calculations. The role played by radical reactions in the corona discharge has been probed by a series of experiments carried out using isotopically labeled reagents and a radical scavenger.

## 2. Experimental Methods

**2.1. Reagents.** Benzene (UV spectroscopy grade), phenol, perdeuterated water, and benzene (purity >99.5%) used in all the experiments were purchased from Fluka. $H_2{}^{18}O$ (Cambridge Isotope Laboratories, Inc.) has a purity of 95%. All reagents were used without any further purification.

**2.2. Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI−MS).** APCI−MS experiments were performed in a Bruker Esquire-LC quadrupole ion trap mass spectrometer (Bruker-Daltonics, Milano, Italy) equipped with an APCI interface (HP/Agilent Technologies). Details of the experimental apparatus have been described previously.[10,13] The nebulizer gas usually employed is high purity $N_2$ obtained from the boil-off of a liquid nitrogen dewar, but in some experiments air is used in order to increase the amount of oxygen with respect to its background level in the corona region. High purity nitrogen is also used as drying gas with a flow of 6 L/min at a temperature of 300 °C. The source region is kept at 450 °C during measurements. Benzene, deuterated benzene, or phenol is introduced as vapor by connecting the headspace of a vial

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containing the pure species with the source environment and flushing with the nebulizer gas. The partial pressure of $C_6H_6$ or $C_6D_6$ is adjusted so that the amount introduced in the source is equivalent to a liquid injection flow of 0.1 mL/min. Some analyses were performed on benzene and deuterated benzene in the presence of excess water (either $H_2O$, $D_2O$, or $H_2{}^{18}O$). In this case water is infused as neat liquid by a micrometric syringe pump (Hamilton) at a flow rate of 0.1 mL/min. In the experiments performed using a mixture of benzene and commercial phenol, the latter was introduced as vapor into the nebulizer inlet, while benzene was injected as liquid by the micrometric syringe. The operating conditions have been optimized to obtain the highest molecular ion abundance in different mass ranges for each compound or mixture under study. The mass spectrometer is operated with a scan rate of 13 000 u/s, and mass spectra collected in the full scan mode are obtained by scanning over the range $m/z$ 50−300. MS/MS experiments have been carried out by resonant activation of the precursor ions by using He gas in the trap, and the corresponding mass spectra represent the average of 5−10 scans. CID (collision induced dissociation) measurements were carried out by changing the amplitude of the rf potential applied across the end caps. Such amplitude has been optimized in order to obtain the maximum total conversion of parent to fragment ions.

**2.3. Guided Ion Beam Tandem Mass Spectrometer (GIB-MS).** Our home-built GIB-MS apparatus allows cross section measurements for reactions of mass-selected ions with neutral molecules.[14] The setup consists of a tandem mass spectrometer equipped with a radio frequency octupole scattering cell. The octupole is placed between the first quadrupole for mass selection of reagent ions and the second quadrupole for mass-selective detection of products. Pressure in the scattering cell can be varied in the range $10^{-7}-10^{-3}$ mbar, and it is measured by using a spinning rotor gauge (MKS SRG2). Ion−molecule reactions of $C_6H_6{}^{+\bullet}$ and $C_6H_5{}^+$ ions with $O_2$ molecules have been studied in the GIB-MS setup. The primary ion beam is produced by electron bombardment (at energies of about 20−30 eV) of a suitable neutral precursor ($C_6H_6$ for benzene radical cations and $C_6H_5Cl$ for phenylium cations). The kinetic energy of reagent ions can be varied by changing the octupole DC potential with respect to the ion source. If the pressure in the cell is sufficiently low to guarantee single collision conditions, the ratio between the measured signal intensities of product and reactant ions is proportional to the reactive cross section.

**2.4. Dielectric Barrier Discharge Plasma (DBD).** Nonthermal plasmas working at high pressure are unstable, easily evolving in an arc. When arcing occurs, temperatures of electrons, ions, and neutral molecules tend to equilibrate. Moreover, arc formation occurs in a narrow spatial region, thus limiting the discharge volume. To avoid arc transition it is necessary to provide a negative feedback between the voltage applied to the electrodes and the current flow. When working at high pressure, the stabilization of the discharge by fixing the current in the circuit is generally ineffective. The alternative is to decrease the discharge duration, "switching off" the discharge prior to the transition into arc. In the case of a "barrier discharge", a dielectric coating on the electrodes accomplishes the stabilization because the accumulation of charges on the dielectric material inhibits streamer propagation.[15]

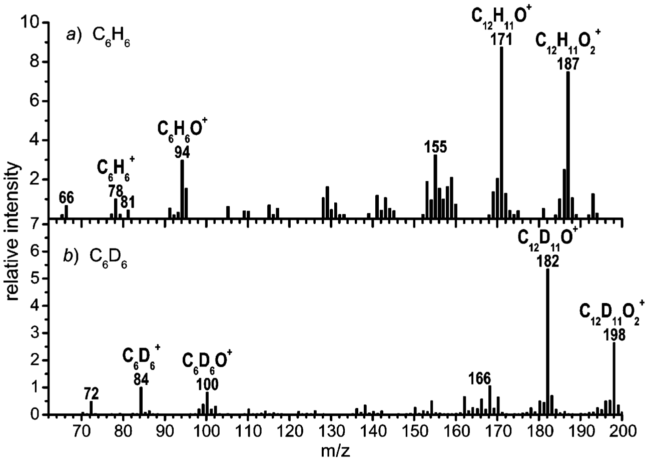

**Figure 1.** Positive ion mode mass spectra from the corona discharge source operating with: (a) benzene and (b) deuterated benzene. Air is used as nebulizer gas in both cases, and benzene injection flow is 0.1 mL/min. Other instrumental conditions are reported in the section Experimental Methods.

Our reactor consists of a quartz tube (diameter = 10 mm) surrounded by a copper outer electrode. The inner concentric electrode is a metallic rod embedded in a ceramic tube (diameter = 3 mm). The length of the plasma system is about 5 cm. The reactor is vacuum sealed to allow control of the gas sample under treatment. Electrodes are powered at 50 Hz by a variable high voltage transformer. The energy transferred to the plasma is evaluated by measuring both the applied voltage (with an HV probe) and the transferred charge (with an HV capacitor in series with the discharge).

Gaseous benzene was admitted from the headspace over the liquid and mixed with $O_2$ and $N_2$ in different ratios. After plasma treatment, gaseous samples were collected and analyzed off-line by GC−MS. The solid material deposited on the reactor walls was dissolved in acetone, and the concentrated solution was analyzed by GC−MS. The chromatograph is a Thermo-Finnigan Trace GC Ultra coupled to a Thermo-Finnigan Trace DSQ quadrupole mass spectrometer. The GC column is a DB5 15 m with an inner diameter of 0.25 mm. The carrier gas flow (He) is 1 mL/min, and the injector and the interface temperatures are 250 °C and 300 °C, respectively. Injection volumes are 1.0 or 2.0 $\mu$L. The temperature program consists of an initial hold at 80 °C for 2 min followed by a linear ramp from 80 to 300 °C at 10 °C/min with a final hold at 300 °C for 5 min. The mass spectra are recorded in the 70 eV EI (electron impact) mode, and the quadrupole mass spectrometer is scanned from $m/z$ 50 to 350 at a rate of 900 u/s.

**2.5. *Ab Initio* Calculations.** *Ab initio* quantum chemical calculations were performed by using Spartan 04 (Wavefunction Inc., Irvine, CA). Geometry optimization for intermediates and transition states was carried out at the density functional level of theory that utilizes the hybrid functional B3LYP[16] and the 6-31G* basis set. In order to get more accurate results, single point energy calculations on the optimized geometries have been carried out at the MP2/6-311+G** level of theory.[17]

## 3. Results

**3.1. Structure and Mechanisms of Phenol Cation Formation from Corona Discharge Experiments.** The most abundant ionic species in the corona discharge mass spectrum of $C_6H_6$, when air is used as nebulizer gas (Figure 1), are observed at $m/z$ 94 ($C_6H_6O^+$), 171 ($C_{12}H_{11}O^+$), and 187 ($C_{12}H_{11}O_2{}^+$). The elemental composition and some structural information on the O-containing products have been determined by (i) deuterium labeling of benzene, (ii) MS/MS experiments performed in the ion trap, and (iii) isotopical H/D exchange reactions observed after $D_2O$ or $H_2O$ addition in the ion source. For the sake of clarity, in the following we focus on the reaction mechanisms

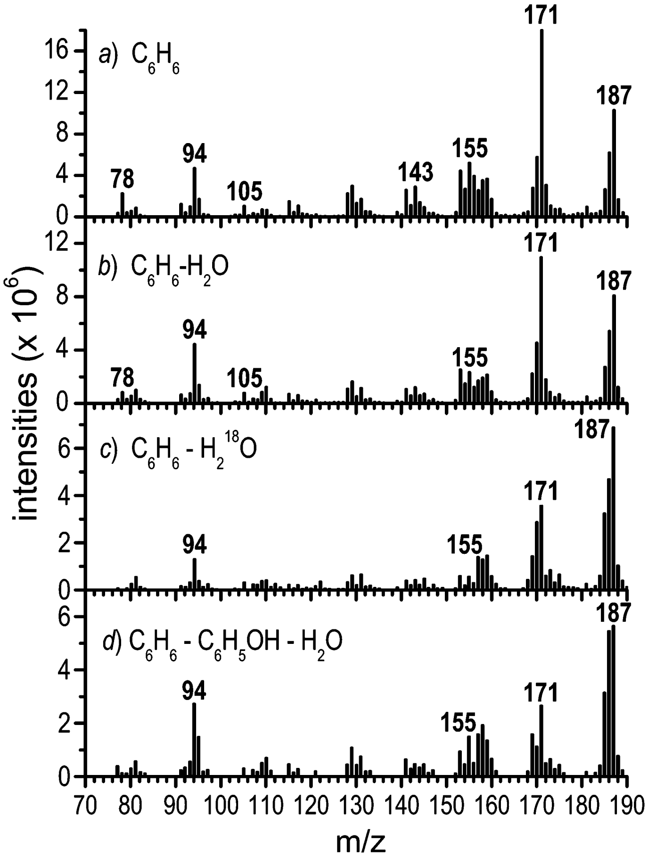

**Figure 2.** Positive ion mode mass spectra of $C_6H_6$ from the corona discharge source: (a) pure benzene injection flow 0.1 mL/min, in air as nebulizer gas; (b) mixture of benzene (injection flow 0.1 mL/min) and $H_2O$, in air as nebulizer gas; (c) mixture of benzene (injection flow 0.1 mL/min) and $H_2{}^{18}O$, in air as nebulizer gas; (d) mixture of benzene (injection flow 0.1 mL/min), phenol (≤ 0.1%), and $H_2O$ in $N_2$ as nebulizer gas.

leading to phenol ion ($C_6H_5OH^{+\bullet}$, *m*/*z* 94). In the negative ion mode corona discharge mass spectrum of $C_6H_6$, the most abundant species is the phenoxide anion $C_6H_5O^-$ at *m*/*z* 93.

The assignment of the peak at *m*/*z* 94 to phenol cation $C_6H_5OH^{+\bullet}$ has been confirmed by observing an *m*/*z* shift to 100 in APCI spectra recorded with perdeuterated benzene (see Figure 1). In addition, the MS/MS spectra of ions at *m*/*z* 94 in $C_6H_6$ and *m*/*z* 100 in $C_6D_6$ show the loss of a neutral species of 28 Da (CO molecule), which is a typical fragmentation route of the phenol ion.[18,19] Furthermore, upon addition of $D_2O$ to $C_6H_6$ or $H_2O$ to $C_6D_6$ in the source, an H/D exchange reaction occurs. Such a process leads to a shift of the phenol ion cluster from *m*/*z* 94 to *m*/*z* 95 ($C_6H_5OD^{+\bullet}$) in the $C_6H_6/D_2O$ mixture and from *m*/*z* 100 to *m*/*z* 99($C_6D_5OH^{+\bullet}$) in the $C_6D_6/H_2O$ one. These findings support the conclusion that ions at *m*/*z* 94 and 100 have the structure of phenol, with the O-bound proton leading to facile scrambling with water.

A series of experiments has been performed in order to investigate the origin of the phenol molecular cation. Its oxygen atom could derive either from molecular oxygen or from humidity water. Concerning $O_2$, when the background oxygen level present in the corona region is varied in the range 0.02−20%, the ratio of the signal intensity at $m/z = 94$ and 78 changes accordingly with the amount of $O_2$. The role of water has been checked by using isotopically labeled $H_2{}^{18}O$ in the corona region. Such an addition does not lead to a substantial $^{16}O/^{18}O$ shift of the relevant ions, as shown in Figure 2a−c. These findings prove that the oxygen atom of phenol ions does not derive from water molecules. In order to rule out the possibility that the ion at $m/z = 94$ might result from in-source fragmentation of heavier O-containing ions (such as $C_{12}H_{11}O^+$ or $C_{12}H_{11}O_2{}^+$), we have carried out in-source CID measurements by changing the voltage applied between the end of the capillary and the skimmer, and we do not observe any significant change in the relative intensity of $m/z = 94$ ion.

The mechanism previously proposed[20,21] for the generation of phenol cations in atmospheric pressure photoionization (APPI) of benzene is based on the attack of benzene radical cations on oxygen molecules:

$$C_6H_6{}^{+\bullet} + O_2 \rightarrow C_6H_6O_2{}^{+\bullet} \rightarrow C_6H_5OH^{+\bullet} + O \qquad (1)$$

This reaction is thought to proceed via the formation of an intermediate adduct of “distonic” nature having the structure of a peroxyl radical cation. Oxygen atom elimination from the intermediate would eventually afford the phenol cation. The adduct ion $C_6H_6O_2{}^{+\bullet}$ at *m*/*z* 110 has been observed in APPI spectra.[20,21] In our APCI spectrum of $C_6H_6$ (see Figure 1) the intensity of ions at *m*/*z* 110 is quite small. We believe that such an ion cannot be attributed to the adduct ion $C_6H_6O_2{}^{+\bullet}$ because a peak of similar intensity at *m*/*z* 110 is observed also in the case of $C_6D_6$, while the expected isotope shift to give $C_6D_6O_2{}^{+\bullet}$ at *m*/*z* 116 is not observed. To the best of our knowledge the gas phase reactivity of $C_6H_6{}^{+\bullet}$ with $O_2$ has been explored solely in a flow tube experiment but no reaction was observed.[22] We have therefore decided to study reaction (1) using the GIB tandem mass spectrometer, and results will be presented in the next section.

An alternative ionic mechanism for phenol formation might be the reaction of phenylium cations with oxygen molecules, according to the following two-step process:

$$C_6H_5{}^+ + O_2 \rightarrow C_6H_5O^+ + O^\bullet \qquad (2)$$

$$C_6H_5O^+ + R-H \rightarrow C_6H_5OH^{+\bullet} + R^\bullet \qquad (3)$$

Using the GIB-MS setup we have studied process (2), and results will be presented in the next section.

**3.2. GIB-MS Results and *Ab Initio* Calculations.** The elementary reactive processes of benzene and phenylium cations with molecular oxygen were studied using the GIB-MS technique, in order to ascertain the feasibility of the above-mentioned ionic routes to phenol cation synthesis. To reproduce the “thermal” collision energy conditions typical of atmospheric pressure sources, experiments were performed at the smallest collision energy obtainable in our apparatus (∼0.2 eV in the center of mass frame) for these systems.

When $C_6H_6{}^{+\bullet}$ is reacted with $O_2$, no evidence is found for phenol cation production (*m*/*z* 94) and for the formation of the adduct ion at *m*/*z* 110 according to reaction (1), even when working at the highest possible pressures in the scattering cell ($\approx 1.3 \times 10^{-3}$ mbar). Experimental data show that the benzene radical cation is practically unreactive with molecular oxygen. To support our experimental findings we performed also *ab initio* quantum chemical calculations on reaction (1). A schematic representation of the doublet potential energy profile and geometries of the relevant stationary points are reported in Figure 3. We find that the adduct $C_6H_6O_2{}^{+\bullet}$ (*m*/*z* 110, indicated as 110_A in the figure) lies 0.6 eV above the reactants $C_6H_6{}^{+\bullet}$ + $O_2$ and is stabilized toward back-dissociation to the reactants by a transition state (T.S.1) of about 0.5 eV. Adduct 110_A can rearrange into 110_B by migration of an H atom from the

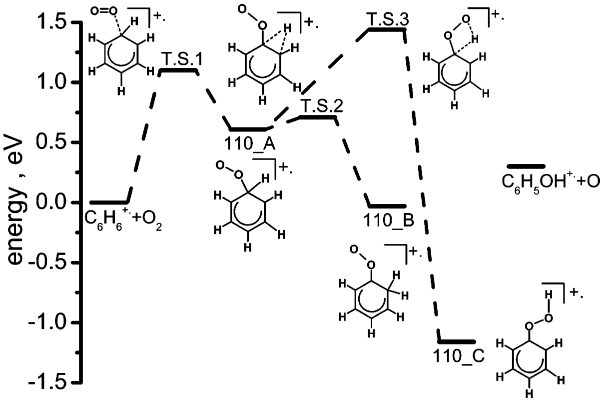

**Figure 3.** Schematic representation of the $C_6H_6^{+\bullet}-O_2$ potential energy profile and geometries of the relevant stationary points. Calculations have been performed at the MP2/6-311+G**//B3LYP/6-31G* level of theory. The dashed lines are only a guide for the eye.

ipso carbon to the adjacent C along the ring via a transition state (T.S.2) and a barrier of 0.1 eV, while isomerization into the most stable peroxyl cation (110_C) is precluded by a barrier of 0.8 eV. According to our calculations, the detection of the adduct (110_A) is unlikely because an initial barrier of about 1 eV needs to be overcome. We thus conclude that reaction (1), previously proposed[20,21] as a viable ionic mechanism for phenol synthesis, is not relevant for the production of the phenol cation.

We have therefore moved to study the reaction of $C_6H_5^+$ with $O_2$. From flow tube experiments it is known that phenylium ions open the following reactive channels with $O_2$:

$$C_6H_5^+ + O_2 \rightarrow C_4H_5^+ + 2CO \tag{4}$$

$$C_6H_5^+ + O_2 \rightarrow C_5H_5O^+ + CO \tag{5}$$

The value of the measured branching ratio for $C_4H_5^+$:$C_5H_5O^+$ is about 9, and the overall rate constant is $k = 5.4 \times 10^{-11}$ cm$^3$ s$^{-1}$, corresponding to a value of $5.4 \times 10^{-12}$ cm$^3$ s$^{-1}$ for the rate constant of reaction (5).[22] When $C_6H_5^+$ is reacted with $O_2$ in the GIB-MS apparatus, we observe, besides the two known channels, a minor channel forming the phenoxy cation $C_6H_5O^+$ via reaction (2) with a branching ratio $C_6H_5O^+$:$C_5H_5O^+$ of about 1:10. Taking the measured rate constant value[22] and using the branching ratio obtained in our GIB-MS experiment, we can estimate a rate constant for phenoxy cation production via reaction (2) of $\sim 5 \times 10^{-13}$ cm$^3$ s$^{-1}$. Once phenoxy cations are formed, the subsequent production of phenol requires the addition of an H atom via reaction (3), most likely from water or benzene. In both cases the reaction is endothermic ($\Delta H° =$ 1.3 eV for R = OH and 1.0 eV for R = $C_6H_5$, respectively, in eq (3), according to the heat of formation of the relevant species given in the literature[23]). On the basis of the endothermicity of process (3) and the small value of the rate constant for reaction (2), it is reasonable to conclude that, on the whole, the reaction of phenylium ions with $O_2$ is not relevant for the production of phenol ions in the corona discharge experiment.

For the sake of completeness, ion molecule reactions involving active oxygen species such as O radicals should also be considered. The reactivity of benzene cation $C_6H_6^{+\bullet}$ with O atoms has been studied already in a selected ion flow tube apparatus,[24] and the measured rate constant is $k = 9.5 \times 10^{-11}$ cm$^3$ s$^{-1}$ at 300 K. The adduct ion $C_6H_6O^{+\bullet}$ is not observed, and a mechanism leading to fast dissociation into $C_5H_6^{+\bullet}$ + CO is proposed on the basis of theoretical calculations.[25] Despite the considerable value of the rate constant, on account of the smaller concentrations of ions and radicals with respect to neutrals, the probability of ion−radical encounters in atmospheric pressure environments should be negligible and therefore it cannot account for phenol production.

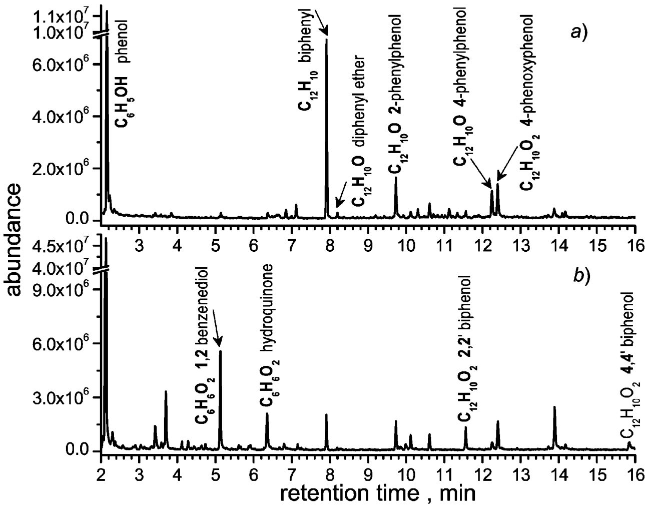

**Figure 4.** GC−MS analysis of the solid deposit (dissolved in organic solvents) after DBD plasma treatment of $C_6H_6$ and $O_2$ in $N_2$ at a total pressure of ∼900 mbar: (a) with $O_2$ concentration ∼4%; (b) with $O_2$ concentration ∼18%.

We have also considered the case in which the charge is not on the benzene moiety but on oxygen-carrier species such as $O_2^+$ and $O^+$ ions. In fact, the latter are known to be produced in a corona discharge in air by electron impact ionization.[9] However, their reactivity with $C_6H_6$ has been shown by flow tube experiments[26,27] to proceed exclusively by rapid nondissociative charge transfer ($k = 1.4 \times 10^{-9}$ cm$^3$ s$^{-1}$ for $O_2^+$ and $k = 1.9 \times 10^{-9}$ cm$^3$ s$^{-1}$ for $O^+$ at 300 K from ref 26). Therefore, phenol cation synthesis from reactions of oxygen ions with benzene can be excluded.

**3.3. Dielectric Barrier Discharge Results: Analysis of Neutral Products.** As well as the detection of ionic species, crucial information on the mechanisms of benzene oxidation in plasmas can be obtained by probing the neutral molecules. Unfortunately, a direct detection of neutral products in the corona discharge source is not viable, but the general features of APCI sources can be investigated in similar atmospheric pressure plasma reactors working in nonthermal conditions. To this purpose, we have treated benzene/nitrogen mixtures with different amounts of $O_2$ in a DBD reactor at a total pressure of about 900 mbar. Two different experiments have been performed: the first one carried out at relatively low $O_2$ concentration (∼4% $O_2$ and 7−8% $C_6H_6$ in $N_2$) and the second at higher concentration (∼18% $O_2$ and 7−8% $C_6H_6$ in $N_2$). Stable neutral products of the gaseous phase and the solid material deposited on the reactor walls have been analyzed off-line by GC−MS. Due to their low vapor pressures, in both experiments the oxygenated aromatic compounds have been found essentially in the solid deposit and have been extracted by organic solvents. GC analysis of such raw extracts is shown in Figure 4. Phenol is always found the most abundant product, together with biphenyl ($C_{12}H_{10}$) and products deriving from the subsequent oxidation of phenol or related compounds. In particular, they have elemental formula $C_6H_6O_2$ (MW = 110 Da), $C_{12}H_{10}O$ (MW = 170 Da), and $C_{12}H_{10}O_2$ (MW = 186 Da). The different isomers corresponding to $C_6H_6O_2$, $C_{12}H_{10}O$, and $C_{12}H_{10}O_2$ molecular formulas have been identified according to their different retention times and mass spectra and have been explicitly indicated in Figure 4. It is quite remarkable that most

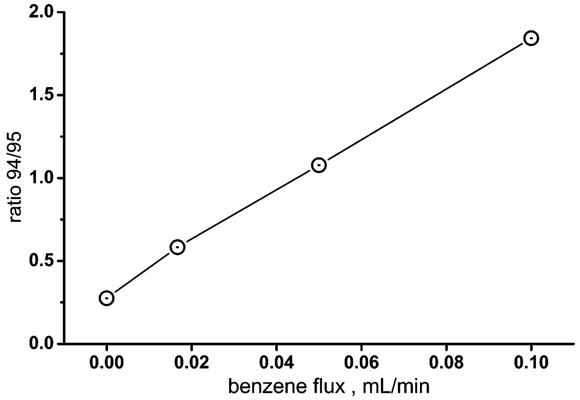

**Figure 5.** Effect of benzene addition on the APCI spectrum of phenol. Commercial phenol is injected as vapor into the nebulizer source while benzene is introduced as liquid from a micrometric syringe at different fluxes. Nitrogen is used as nebulizer gas. The ratio of ion intensities at *m*/*z* = 94 and 95 is plotted against the benzene flux.

of the species observed as ions in the corona discharge spectrum are also observed as neutral molecules (i.e. $C_6H_5OH^{+\bullet}$ and the ions at *m*/*z* 171 and 187, which correspond to protonated $C_{12}H_{10}O$ and $C_{12}H_{10}O_2$, respectively) in DBD.

## 4. Discussion

The outcome of the experimental results so far reported can be summarized as follows:

(i) Phenol radical cations can be synthesized in a corona discharge of benzene and $O_2$.

(ii) The mechanism leading to $C_6H_5OH^+$ is not the previously proposed one[20,21] based on the reaction of benzene cation with $O_2$, as shown by our GIB-MS results and theoretical calculations.

(iii) None of the conceivable alternative ionic mechanisms can be invoked to explain phenol cation formation.

(iv) Neutral phenol is the most abundant among low molecular weight products observed after treatment of $C_6H_6/N_2/O_2$ mixtures in a DBD plasma.

The concurrent detection of O-containing neutral and ionic species in nonthermal plasmas suggests that abundant ions, like $C_6H_5OH^{+\bullet}$, result from the ionization of neutral molecules formed by radical reactions. If this were the case, one would expect that our mass spectra should be comparable to the typical APCI spectrum of phenol, in which the protonated ion (generated by proton transfer with $H_3O^+$) is more abundant than the molecular cation (produced by charge transfer with primary $N_2^+$). On the contrary, as shown in Figures 1 and 2, we observe that the intensity of protonated phenol ions is generally smaller than that of phenol molecular cations. In order to solve this discrepancy, we have carried out APCI measurements with deliberately added phenol, both as a pure substance in the nebulizer gas and in solution with different amounts of benzene. We have detected both 94 and 95 ions, with a ratio depending on the relative content of phenol and benzene. A typical spectrum of a benzene/phenol mixture with a phenol content ≤0.1% is reported in Figure 2d; by changing the benzene molar fraction at constant phenol amount, an enhancement of the ratio 94/95 is observed, and results are shown in Figure 5. The explanation of this finding is based on the competition between two different mechanisms for phenol ionization: charge transfer with $C_6H_6^{+\bullet}$ producing ion at *m*/*z* = 94, and proton transfer with $H_3O^+$ giving protonated phenol at *m*/*z* = 95. When benzene is present in large molar excess, the charge transfer channel is favored over the proton transfer one. Moreover, benzene molecules may build up a hydrophobic cage that segregates phenol molecules and inhibits the proton transfer channel.

We have already anticipated that phenol detected either as ions in the APCI corona discharge or as neutral molecules in the DBD plasma is likely to be produced by a radical chemistry. The chemistry of radicals is usually invoked to explain processes responsible for the oxidation of benzene.[28−30] In particular, radical mechanisms have been proposed to explain the formation of phenol in air−benzene plasmas.[2−5,31,32] Moro-oka has discussed the hydroxylation of aromatics by active oxygen species, with particular reference to atomic O ($^3P$).[1]

In corona and dielectric barrier discharges, a relevant fraction of atomic oxygen is likely to be produced mainly by electron impact dissociation of $O_2$, even though other routes cannot be ruled out. In particular, O atoms are known to be widely involved in the ozone chemistry, and the production of ozone in our atmospheric pressure barrier discharge is well established. We have no direct way of measuring the density of O atoms under our experimental conditions, but a rough estimate of their order of magnitude can be obtained from literature values. In inductively coupled oxygen-containing plasmas they can represent about 2−10% of $O_2$.[33] Even higher densities (up to $5.4 \times 10^{15}$ cm$^{-3}$, corresponding to 58% of $O_2$ dissociation) were measured for a pulsed DC low pressure discharge in air.[34]

A conceivable radical route to phenol synthesis in our nonthermal plasmas would be the gas phase reaction of O atoms with benzene. Such a reaction has been amply investigated in flow systems,[35,36] and the main reactive channels are the following:

$$C_6H_6 + O^\bullet \rightarrow C_6H_5O^\bullet + H^\bullet \qquad (6)$$

$$C_6H_6 + O^\bullet \rightarrow C_6H_5OH \qquad (7)$$

The rate coefficients for the overall process at 400 K have been measured to be in the range $k = (1.1-1.4) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[37,38] Cross section measurements[39] and theoretical calculations[40,41] have shown that the initial step is electrophilic addition of the O ($^3P$) atom to the benzene ring to form a triplet diradical adduct. A recent calculation[40] of the triplet potential energy surface indicates that the rearrangement of the latter into phenol should be a minor channel due a high barrier for 1,2 H shift, whereas the production of phenoxy radical or formylcyclopentadiene should dominate the overall reactivity. We rule out that the peak observed in APCI−MS at *m*/*z* 94 is due to formylcyclopentadiene on the basis of the different fragmentation pattern in the mass spectra. In fact, formylcyclopentadiene is expected to give an intense $[M - H]^+$ peak at *m*/*z* 93 and a peak at *m*/*z* 65 due to HCO loss. We do not observe such fragment ions both in the source and in the MS/MS spectra. Additionally, the mass cluster around *m*/*z* 94 and the MS/MS spectrum of the latter ion in the APCI−MS spectrum of commercial phenol are practically identical to those produced by plasma oxidation of benzene. The presence of phenol in the DBD plasma is confirmed by the matching of retention time in the GC spectra with a commercial standard, by its electron impact mass spectrum, and by NMR analysis. Since $C_6H_5OH$ observed in our experiments has to be in the ground singlet state, if phenol is produced by reaction (7), an intersystem crossing to singlet phenol should occur efficiently. Alternatively, reactivity of metastable O($^1D$) atoms with benzene should play a role.

A complementary mechanism might involve a series of processes initiated by the reaction of phenyl radicals with oxygen, as already reported in ref 29. The potential energy surface for the reaction of $C_6H_5^\bullet$ with $O_2$ has been investigated recently.[42] The reaction starts with an exothermic barrierless addition of $O_2$ to the phenyl radical to produce phenylperoxy radical, which may lose the terminal O atom to yield the phenoxy product:

$$C_6H_5^\bullet + O_2 \rightarrow C_6H_5OO^\bullet \rightarrow C_6H_5O^\bullet + O^\bullet \tag{8}$$

In our plasmas, $C_6H_5^\bullet$ can be generated either by electron dissociation of $C_6H_6$ or by H abstraction reactions on benzene by suitable species, such as OH or H radicals.[2-5]

Once phenoxy radicals are formed by either process (6) or (8), the production of phenol cation under corona discharge conditions could occur via proton transfer reaction with hydronium ions:

$$C_6H_5O^\bullet + H_3O^+ \rightarrow C_6H_5OH^{+\bullet} + H_2O \tag{9}$$

Due to the high proton affinity of phenoxy radical (8.89 eV[23]) the above reaction is exothermic ($\Delta H^\circ = -1.73$ eV) and therefore could be relevant in the presence of the ubiquitous $H_3O^+$ ion. However, if this were the case, the corona discharge mass spectrum of perdeuterated benzene would show a major peak at *m*/*z* 99 attributable to $C_6D_5OH^{+\bullet}$ from reaction (9). Conversely, in our spectrum (see Figure 1b) a signal at *m*/*z* 100 ($C_6D_5OD^{+\bullet}$) represents the most abundant ion in the cluster of peaks around mass 100 Da, and therefore it cannot occur from protonation of phenoxy radical. In addition, the deuterium abstraction from $C_6D_6$ by $C_6D_5O^\bullet$ is an endothermic process ($\Delta H^\circ = 1.1$ eV according to the heats of formation reported in ref 23). Therefore, the origin of $C_6D_5OD^{+\bullet}$ ion can be explained only by assuming that a 1,2 deuterium shift in the $C_6D_6O$ adduct leads to neutral perdeuterated phenol from which phenol cations are subsequently produced by charge transfer with the primary $N_2^+$ and $O_2^+$ ions or with the secondary abundant ion $C_6H_6^{+\bullet}$, because the IP of phenol (8.49 eV[23]) is lower than that of benzene itself (9.24 eV[23]).

As far as the production of phenol in the DBD plasma is concerned, the phenoxy radical could be quenched into phenol by the following reactions:[29]

$$C_6H_5O^\bullet + H^\bullet \rightarrow C_6H_5OH \tag{10}$$

$$C_6H_5O^\bullet + HO_2^\bullet \rightarrow C_6H_5OH + O_2 \tag{11}$$

It has been proposed also that the oxidation of benzene, at the low temperatures typical of atmospheric conditions, proceeds by a mechanism initiated by the reaction of $C_6H_6$ with OH radicals giving the hydroxycyclohexadienyl radical c-$C_6H_6$−OH.[43] The latter species then reacts with $O_2$, giving phenol and $HO_2$, but this reaction is fairly slow (the calculated rate constant is $k = 1.4 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at $T = 298$ K) and therefore should not be relevant in our experimental conditions. Irrespectively of the relative rates, such a mechanism will imply that the O-bound hydrogen atom derives from an external source (i.e. water from air humidity). Therefore, in the case of $C_6D_6$ oxidation, the production of $C_6D_5OH$ would be expected. Once again this mechanism is not in agreement with the benzene/air APCI mass spectrum, in which the perdeuterated $C_6D_6OD^+$ ion has been observed.

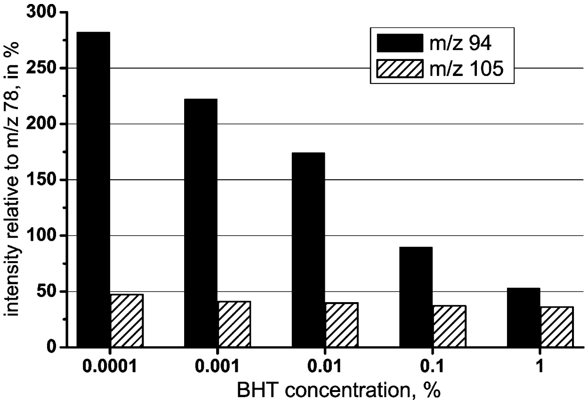

**Figure 6.** Effect of the addition of the radical scavenger butylated hydroxytoluene (BHT) on the intensities of the ions at *m*/*z* 94 (phenol cation) and *m*/*z* 105 (benzenediazonium ion) detected in the corona discharge plasma of benzene and air mixtures.

To directly probe the role played by radicals in the production of phenol ion, we carried out a series of experiments by introducing, into the corona discharge source, solutions at different concentrations of the radical scavenger butylated hydroxytoluene (BHT) in benzene. Mass spectra were recorded as a function of the BHT concentration from 0.001% to 1%, and results are presented in Figure 6. The addition of BHT decreased the intensity of phenol with respect to benzene radical cation, and such a decrease was higher at larger BHT concentrations. In particular, the intensity of ions at *m*/*z* 94 decreases by a factor of ~5, whereas the intensity of the $C_6H_5N_2^+$ cation at *m*/*z* 105 is not affected by the presence of BHT in the plasma. Since benzenediazonium ions are produced in the nucleophilic addition of $C_6H_5^+$ to $N_2$,[10,44] these results strongly support the hypothesis that BHT suppresses selectively the radical chemistry but does not interfere significatively with the ion chemistry.

## 5. Conclusions

This paper deals with the production of phenol in atmospheric pressure plasmas of benzene−air mixtures, and we have pursued this goal by investigating both the ionic and neutral species produced therein. In particular, we have studied the ions generated in a corona discharge source by mass spectrometry techniques, whereas neutral species formed in an atmospheric pressure dielectric barrier discharge of benzene and air have been detected by gas chromatography−mass spectrometry. Remarkably, the O-containing neutral molecules detected in the GC spectrum mirror the main ionic peaks observed in APCI experiments, suggesting a common route of synthesis. With reference to the ionic products, we have identified the ion−molecule reactions conceivably producing the phenol cation and we have investigated the most relevant ones both experimentally, in a guided ion beam tandem mass spectrometer, and theoretically, by *ab initio* calculations. Our investigation suggests that ionic mechanisms do not play a significant role in the production of $C_6H_5OH^{+\bullet}$. Experiments carried out with isotopically labeled $H_2{}^{18}O$ demonstrate that the oxygen atom of the phenol molecule does not come from water. In further tests performed either by diminishing the $O_2$ content or by adding BHT (an efficient radical scavenger) to the corona plasma, we observe a remarkable decrease of the phenol cation, pointing to a fundamental role of atmospheric $O_2$ activated by the discharge. Together, these observations indicate that, in the plasma-induced oxidation of benzene at atmospheric pressure, phenol molecules result from a radical chemistry through a formal insertion of oxygen in the C−H bond. Our conclusions review the widely accepted assumption that ions in APCI sources are generated only by fast ion−molecule reactions. In particular conditions, some of the ionic species may be produced by radical reactions and this finding could be used to increase the selectivity of APCI sources.

In the case of benzene/oxygen mixtures the relevant role played by radicals is a consequence of both the presence of highly reactive O species and the absence of efficient ionic routes to phenol production. Differently, in the case of benzene/nitrogen mixtures the balance between ionic and radical mechanisms favors the former and benzenediazonium ion is observed as the product of the reaction of $C_6H_5^+$ with $N_2$.[10]

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