THE CORONA DISCHARGE IN HUMID AIR AS AN OXIDIZING TOOL FOR THE DESTRUCTION OF AROMATIC SOLUTES.

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Abstract

The neutrals generated in a point-to-plane type corona discharge in humid air are good oxidizing agents towards solutes in aqueous medium. These chemical properties are checked on a series of inorganic solutes including iron derivatives in the case of a negative D.C. discharge, and later applied in the case of an A.C. discharge to the oxidizing destruction of organic solutes. The relevant tested molecules are phenol derivatives of special interest as major pollutants or parent molecules for weed-killers, defoliants or pesticides. The destruction rates are linear functions of the quantity of electricity involved in the treatment. In addition, a multi-step mechanism is proposed for the degradation kinetics.

Introduction

The activated heavy species created at the point electrode in a typical point-to-plane corona discharge (i.e., the anions, the cations and the chargeless or neutral species) are in part responsible for the collective chemical properties of the plasma which are operated in most of the plasma treatments. It's fundamentally interesting to determine the own part of each kind of species to understand better the existing processes and to elaborating improved new ones.

This led us to separate the flux of the ions from that of the neutrals. Since we focused on the chemical properties of the activated neutrals, we trapped the ions by means of an earthed ring electrode [1]. Its inner diameter is convenient for good ion trapping and subsequently for a good separation, and large enough to allow no diffraction of the neutrals, so that they are then all able to react with a target disposed under the ring. By this way our approach is completly different from the interesting one of Tezuka et al.[2,3] who performed a mere electrolysis process by setting the anode in the solution.

The chemical properties of the neutrals generated in a corona discharge are examined in terms of oxidation-reduction reactions, since reactions of this type take place in particular surface treatments such as the increase in the wettability of polymer materials. For our demonstrative purpose we selected a water-saturated air plasma and aqueous solutions as the exposed targets.

Preliminary experiments were performed with D.C. negative discharges on potassium iodide and on a series of Fe(II) derivatives dissolved in water: Mohr salt [i.e., $FeSO_4.(NH_4)_2SO_4$], potassium hexacyanoferrate(II), ferrocene [i.e.,biscyclopentadienyl Fe(II)] and ferroïn [i.e., tris(1-10 phenanthroline) Fe(II)].

We improved our work by examining particular organic solutes selected among the phenol family, so that we report also here on their treatment by the neutrals of an A.C. corona discharge and on their resulting oxidizing destruction. The phenols were selected on the basis of ecological considerations since such molecules are listed as major pollutants of the ground waters. For instance the trichloro-2,4,5 phenol was involved in the formation of dioxin in the Seveso disaster. This chemical is also well known as a starting material for numerous weed-killers (e.g. substituted Trichloro-2,4,5 anisole), defoliants (e.g. substituted Dichloro-2,4 anisole), pesticides or bactericidal toiletries (e.g., hexachlorophene). Even at low concentrations the parent molecule is responsible for the bad taste of phenol-containing waters.

Experimental

The already described [1] corona device used in this study slightly differs from the classical point-to-plane device. Since the neutrals are the prominent heavy species responsible for the oxidizing chemical reaction involved in the treatment, it is convenient to separate their flux from that of the ions, and this is performed by trapping the charged species. The trapping is realized by means of an earthed ring electrode centered along the axis of the rod which is raised to the HV potential and acts as the active electrode. The trapping efficiency of the device was verified from electrical measurements. Besides this new device was found superior to the classical device using a trapping grid since no diffraction of the neutrals by the metallic electrode can take place.The current sources used for the study were either a 30 kV D.C. or a 15 kHz A.C. generator, with stainless steel electrodes (a point and a ring) raised to the convenient ddp.

The solutions are prepared from commercially available analytical grade chemicals purchased from Aldrich, except the potassium picrate and the bis(1-10 phenanthroline) Fe(II) which were prepared at the laboratory and analysed satisfactorily. The concentrations of the solutes were determined immediately after the plasma treatment by conventional spectrophotometric or electrochemical methods. For the study of the oxidation of phenol in acid medium, a coloured diazo derivative was formed according to the standard procedure.

Results and Discussion.

a- Preliminary results

Various inorganic solutes in aqueous solutions were oxidized when exposed to the flux of the neutrals in a negative discharge in air. Iodide turned into iodine, and a series of iron(II) derivatives (i.e., $FeSO_4.(NH_4)_2SO_4$, potassium hexacyanoferrate(II) and ferrocene) were also completely oxidized. However, the red color of the ferroïn complex didn't disappear, so that the complex remained in the reduced form for the main part, and only small quantities of the pale blue oxidized ferriin were formed.

These results demonstrated that exposure to the gaseous neutrals species induced oxidizing effects on the solutes in the condensed medium. From a thermodynamic point of view, the ability to oxidize an aqueous solute is related to its normal oxidation potential E° (V/NHE) in water. This explains why I^- (E° = 0.54), Fe^{2+} (E° = 0.77), $Fe(CN)_6^{4-}$ (E°= 0,36), ferrocene (E° = 0.40) are readily oxydized, since their normal potential is rather low. The potential of ferroïn is much higher (E° ≈ 1,15), and very close to that of water (E°= 1.23), which leads to conclude that water is oxidized nearly as easily as ferroïn.

These preliminary experiments state two important results: i) the neutrals created in the gas phase are able to oxidize solutes in water and ii) they behave as very strong oxidizers.

The kinetic approach of the oxidation reactions was also considered since it implies a biphasic process which cannot be simple. The removal of the reduced species or the formation of the oxidized form were followed as a function of the treatment time. The overall oxidation kinetics was found to obey a pseudo 1st-order law; for example the kinetic constants relevant to the oxidation of Fe^{2+} and $Fe(CN)_6^{4-}$ were respectively 0.72 10^{-4} s^{-1} and 3.30 10^{-4} s^{-1} for a treatment performed at 100 μA.

b- A. C. corona treatment of phenol C_6H_5OH.

When exposed to the neutrals of an A.C. corona discharge in air, aqueous acid or basic solutions of phenol are oxidized up to the formation of CO_2, according to a mechanism which depends on the experimental conditions.

In alkaline solutions, the evolution of the spectra with exposure to the neutrals is complicated (Fig. 1A) since a series of absorption bands (e.g., 318 nm, 263 nm) appear and then disappear, while the intensity of someones remains constant for more than half an hour (e.g., 287 nm) and that of other bands decrease (e.g. 234 nm). Such an evolution evidences the occurrence of a multisteps kinetic scheme. The decrease of the 234 nm band obeys an overall pseudo first order law and is ascribed to the degradation of phenate. Besides, the relevant kinetic constant depends on the current intensity and linearly increases with I (Table 1) with a proportionality coefficient close to 0.52 10^{-3} ($min^{-1}.\mu A^{-1}$).

The spectrum of the starting solution moves from that of pure phenate (phenol was dissolved in 0.01M soda solutions) to that of a mixture phenate/phenol for the very first minutes of the treatment. This is in agreement with the known [4] acid effect induced by the neutrals, but due to the large excess of base in the starting solutions, the pH change is limited in our working conditions. However this doesn't prevent to consider the phenate/phenol equilibrium which may be involved in the mechanism of ring opening as a pre-equilibrium step. This argument is backed up by the absorption spectra of solutions treated for more than 15 minutes which exhibit a set of bands around 320 nm which can be attributed to a mixture of dihydroxy benzene derivatives (i. e., $C_6H_4(OH)O^-$ and the conjugated acid $C_6H_4(OH)_2$).

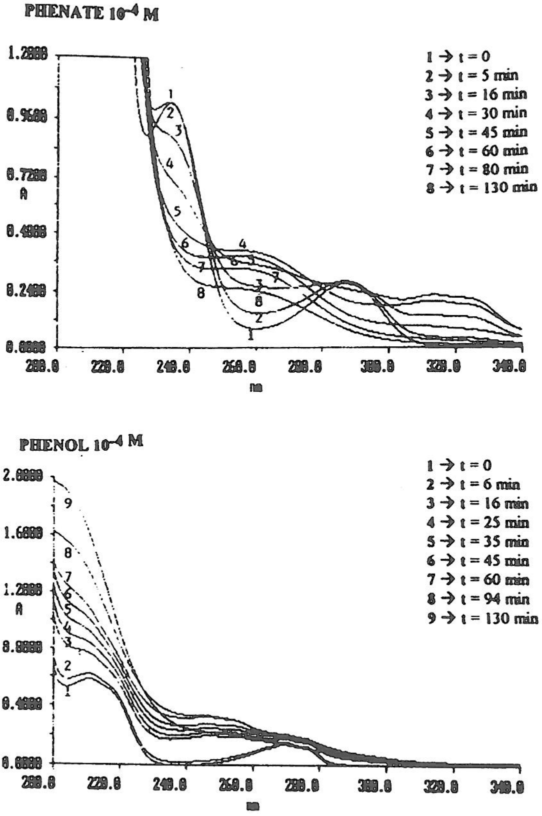

Fig. 1- Evolution of the spectra of 10^{-4} M phenate (A) and phenol (B) aqueous solutions with exposure duration to the neutrals of an A.C. Air Corona discharge.

The transient formation of Nitrites and that of Nitrates were already studied [4] but their main absorption bands (360 nm, 280 nm, 210 nm and 313 nm respectively) did not interfere, except for the high energy band.

The formation of highly oxidizing species in the discharge may be considered as a reasonable starting assumption, and the occurrence of radicals such as OH° may be taken into account since it takes place in humid air. Such species are known to oxidize nitrites. They may also oxidize phenol by ring opening and yield dicarboxylate salts up to oxalate and at least carbonate, all chemicals absorbing in the far UV range (2,4-hexadiene absorbs at 227 nm). In addition, HPLC analysis evidenced a mixture of several dicarboxylate salts which could not however be yet identified.

An overall oxidation mechanism may then be proposed as the following scheme which takes into account the fact that olefinic molecules can be cracked in a corona discharge: $C_6H_5O^-$ (phenate) + H^+ = C_6H_5OH (phenol)

$C_6H_5OH + OH°$ --> ["A"] --> [^-O_2C- CH=CH-CH=CH-CO_2^-] (muconate) --> (maleate / fumarate) + (succinate) + (malonate) + (oxalate) --> (formiate) + (carbonate)

In addition, the transient fixation of OH° radical on the aromatic ring may be related to the first step of this scheme according to the fast reactions observed in pulse radiolysis and yielding the dihydroxy derivatives "A".

An alternative way refers to the ozonization of phenol in aqueous media [5] since ozone is generated in the discharge.

The overall pseudo-first order destruction of phenol may be related to the diffusion of OH° or ozone from the gas phase into the solution.

In acid solutions, the spectrum of the phenol solution (Fig. 1B) shows after an exposure of a few minutes a mixture of dihydroxy derivatives as intermediates in the overall degradation process, and this is in agreement with the evolution observed for the alkaline solution.

c- Treatment of some phenol derivatives

The experiments on phenol were extended to selected substituted derivatives in order to investigate the ability of the treatment to remove phenols from phenolic wastes and limit the classical use of chlorine. In fact, the occurrence of phenol is not considered as crippling on the basis if its own toxicity (e.g. the toxicity limit of phenol towards Esch. coli is superior to 100 $mg.L^{-1}$ and it falls to 8 $mg.L^{-1}$ for the amino-4 phenol), but rather on its ability to yield chorophenols.

We report here on typical examples to illustrate the general feature of the treatment. We selected various 2,4,6 trisubstitued phenols (e.g., triiodophenol or trinitrophenol, the latter chemical being not biodegradable) to consider molecules hindered in the reactive o- and p- positions.

The treatments of alkaline solutions of triiodo-2,4,6 phenate or picrate by the

I(μA)	10	16	20	30	40	46	50	55	56	125
---			10.4	16.2	20.8					
Triiodo			3.5		7.1		9.4			
Trinitro	.7	.92				2.9		3.45	3.62	8.4

Table 1- Values of the kinetic constants 1000.k(min^{-1}*) for fixed current intensities (μA).*

neutrals af an A.C. corona dicharge evidence that the disappearance of the phenates follows a pseudo 1st-order kinetic law. and the kinetic constants are also linear functions of the current intensity (Table 1).The slope of the straight lines k(min^{-1}) *vs.* I(μA) are 0.188 10^{-3} and 0.067 10^{-3} for the triiodo 2,4,6 phenate and the picrate respectively. The destruction of the iodo- derivative is much faster than that of the nitro-one. and both reactions are slower than that of the parent molecule. This may be related to the sizes of the molecules since the electron transfers involved in the ring breaking are affected by the volume of the substituant group.

Other molecules in the series are also destroyed under exposure to the neutrals of an air discharge. Similar results are obtained relevant to a fully substituted phenol or more complicated structures. At this juncture, the pentachlorophenol may retain attention as a typical molecule showing two chloro- groups in a p- position. and hence well known as a major pollutant. The removal of this phenol is again a pseudo- 1st order kinetic and the relevant constant k (min^{-1}) is found directly proportional to the current intensity ($k = 0.323\ 10^{-3}$. I (μA)). Another interesting example is given by the degradation of picrylaniline which is slow and leads to picrate in a first step.

Conclusions

The various examples herein reported evidence the properties of the neutrals generated in a corona discharge in humid air which behave as strong oxidizers towards solutes. The relevant mechanism is complicated and remains to be precised since it involves a biphasic process. However a series of phenol derivatives were degraded. giving evidence that the discharge may be conveniently used for the treatment of waste waters. first as an additional way to the biodegradation of the phenols. and with a larger efficiency for the complete removal of non biodegradable chemicals such as picrates.

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