

PLASMA DEGRADATION OF ORGANIC COMPOUNDS OXIDATION OF 1,4-DIHYDROXYBENZENE

N. BELLAKHAL, J.-L. BRISSET

*Laboratoire d'Electrochimie, UFR des Sciences et Techniques de l'Université de Rouen,
76821 Mont-Saint-Aignan Cedex, France*

(Soumis en janvier 1999, accepté en mai 1999)

ABSTRACT : 1,4-Dihydroxybenzene (hydroquinone) is selected as a model molecule to investigate the oxidising properties of a low pressure inductively coupled oxygen plasma discharge on organic powders. The formation of 1,4-benzoquinone and acids is observed as intermediates in a complex mechanism which ultimately yields carbon dioxide. The main steps of the oxidation process are given with the relevant kinetic constants. The influence of the discharge parameters is considered. The technique appears to be efficient for the ageing study of organic powders.

Key words : Non-thermal plasmas; Oxygen; Low pressure electric discharge; Oxidation; Dihydroxybenzene.

RESUME : Le dihydroxy-1,4 benzène est choisi comme molécule modèle de composés organiques pulvérulents pour tester les propriétés oxydantes d'un plasma d'oxygène non thermique à couplage inductif. Le processus d'oxydation, complexe, fait apparaître la 1,4 benzo quinone et des acides comme intermédiaires et les vitesses de certaines étapes ont pu être déterminées. L'influence des principaux paramètres de traitement a été examinée.

INTRODUCTION

Degradation of organics is presently among the topics of major importance since it is involved in most of the pollution removal treatments for water and air. The question is also closely related to the ageing studies which are directly concerned with the food and drug industries. As a consequence, the Advanced Oxidation Processes (AOP) which involve the use of activated matter to perform oxidation reactions widely develop at the moment and share this feature with other techniques such as radiolysis (1), photochemistry, gas phase chemistry (2), sonochemistry (3) and plasma chemistry (4).

The electric discharges are among the most popular ways to generate the activated species present in a plasma. An energy transfer of a few eV takes place between the electric field and the gas phase and raises a part of the gaseous molecules to some rotational, vibrational or electronic excited state. This confers on them an enhanced reactivity due to a new distribution of the electrons on the orbitals in addition to a new polarisation moment induced by the electric field.

The range of the applications of the plasma techniques enlarges everyday, mainly in connection with electronic and material sciences. They are based on the interactions of plasmas with solids (i.e., mostly metals and organic polymers) and are of major importance for surface modifications and for the elaboration of barrier layers : etching, nitriding, deposition, etc..... are widely used processes.

However, most of the plasma surface treatments involve puzzling mechanisms due to the variety and the population of the gaseous reactive species, and also to the variety of products.

Contrary to organic material and polymer plasma treatments (5), plasma organic chemistry is not yet widely developed (6-8), and in particular few authors are interested in plasma treatments of organic liquids (9-11). However it presents several aspects of major importance, for example, the plasma synthesis and the plasma treatment of wastes. Among the salient features of plasma synthesis, we find for example the deposition of diamond like layers. The destruction of wastes by plasma torches concerns numerous pollutants. The removal of toxic molecules and of Volatile Organic Compounds are also good emerging examples for the plasma treatment of wastes and all the techniques relevant to plasma pollution control. Additionally, it is possible to develop a particular plasma chemistry, the aim of which is to transform and add value to molecules by creating functional groups. This chemistry involves the classical reactions: oxidation-reduction, acid-base and radical reactions. We focused on oxidation reactions, and we used a low pressure inductively coupled oxygen plasma generated by a RF electric discharge. We also selected an organic compound in the physical form of a powder as a suitable target for the present study, so that we report hereafter on the oxidation of an organic powder by an oxygen plasma.

A limited number of studies deal with powders, except to prepare sintered materials. We selected organic powders as suitable targets to precise the mechanisms involved in an oxidising treatment performed in a RF inductively oxygen discharge. The plasma device was already used (12) for studying the oxidation mechanism of metals (i.e., copper, zinc and their alloys, nickel) and the relevant spectroscopic studies of the plasma performed on that occasion showed that only the species O and O⁺ could be detected at our working conditions and in the spectral range investigated (12). The oxygen atom was identified by the emission lines at 777.4 nm (triplet state O(³P)) and at 844,6 nm (singlet state O(¹P)). The dissociation degree of the plasma was then estimated around 10%, and the oxidizing power was attributed to the oxygen atoms ($E^{\circ}(\text{O gas}/\text{H}_2\text{O}) = 2.43 \text{ V/Normal Hydrogen Electrode, NHE}$).

Cold plasma treatment of aromatics was already investigated by several authors who worked either on chemicals condensed at low temperature (6, 9, 10) or on vapours mixed to the plasma gas (13). Some of them were concerned with oxygen plasmas (9,13) : all agree with the degradation of the starting chemical. We developed in the laboratory a particular approach which brought us some preliminary experience on the "advanced oxidation processes" based on the plasma techniques since we exposed phenol and phenol derivatives dissolved in aqueous solution to the flux of the neutral species generated in a corona discharge in humid air (14). We observed at the corona conditions (i.e., at atmospheric pressure and ambient temperature) the complete degradation of the organic solutes (even in the case of non-biodegradable substituted phenols). The overall pseudo first order rate constant was related to the current intensity for each tested chemical. A proposed mechanism involves the occurrence of the OH[•] and O₂H[•] radicals provided by the discharge in humid air, in addition to the other strong oxidizers (such as ozone and hydrogen peroxyde also formed in the discharge).

Since the reactivity of oxygen atoms with aromatic compounds is described (11), and especially the reaction of O with double bonded molecules (15) or the attack at the C-H bonds leading to alcohol functions (16), the exposure of a diphenol to an oxygen plasma was expected to lead to various products. We selected the 1,4-dihydroxybenzene (commonly called hydroquinone, H₂Q) as a model molecule to examine the oxidation mechanism of an organic molecule in our RF plasma device. It is known that the phenol function easily oxidises to carbonyl function : in the present case, the 1,4-dihydroxybenzene first yields the 1,4-benzoquinone (Q) as a transient species. In addition to our fundamental purpose, which is to improve our knowledge of the oxidation mechanism under plasma conditions, our study performed on a simple model molecule is intended to provide information on the ability of the plasma technique to help to model the ageing processes of organic powders.

EXPERIMENTAL

A scheme of the plasma reactor is given in Fig 1 which describes a classical RF inductively coupled plasma device. The plasma is created in a silica reactor (i.e., a tube 0.1 m in diameter; 0.3 m in length) by a 13.56 MHz generator fitted with a 7-turn coil. The low pressure is sustained by a mechanical primary pump. The oxygen flow rate J is controlled by a MKS pressure transducer (type 122 A) in the 0-1000 Pa pressure range.

Weighted quantities (around 110 mg) of analytical grade 1,4-dihydroxybenzene (H₂Q) were gently compacted as circular pellets, then disposed on a thin coverglass and tightly positioned normally to the gas flow on a water-cooled stainless steel quenching head. The temperature of the quenching head was measured and never exceeded 308 K, so that it is reasonable to admit that the temperature of the organic sample is constant around the same value.

The treatment conditions may be varied, and the basic key parameters are the injected electric power P, the gas pressure p, the oxygen flow rate J and the distance d between the target and the first coil. We report here on experiments performed at P = 60 W; p = 210 Pa; J = 4.17 m³(1bar, 298 K)s⁻¹ and d = 20 cm as standard conditions. Other conditions, such as a higher power or a reduced distance lead to quicker decomposition of the chemical.

After exposure to the plasma, the organic substance was weighted. An aliquot was dissolved in a (1M) KCl solution to be analysed by voltametry. The current-potential plots were recorded on a PAR 273 potentiostat associated with an IBM PC. The mean current intensities of the oxidation and reduction waves were measured and this allowed us to determine the concentrations of 1,4-dihydroxybenzene (hydroquinone, H₂Q) and 1,4-benzoquinone (Q) respectively. In addition, special sets of experiments were needed to confirm the occurrence of C=O groups in the reaction products by FTIR spectroscopy (Perkin-Elmer 1600). We also used GC analysis (Varian; equipped with a Restek RTX 5 column) so that we could identify maleic and oxalic acids by means of their dimethyl esters.

RESULTS AND DISCUSSION

Preliminary experiments performed on 1,4 dihydroxybenzene pellets exposed to the oxygen plasma showed that the organic compound degrades, as its mass rapidly decreases. (Table1).

t (min):	0	5	10	15	20	25	30	35	40
Δm (g):	0	0.023	0.047	0.052	0.056	0.064	0.071	0.078	0.080

Table 1: Mass decrease Δm of a sample exposed to the plasma ($P = 60W$; $d=20$ cm)

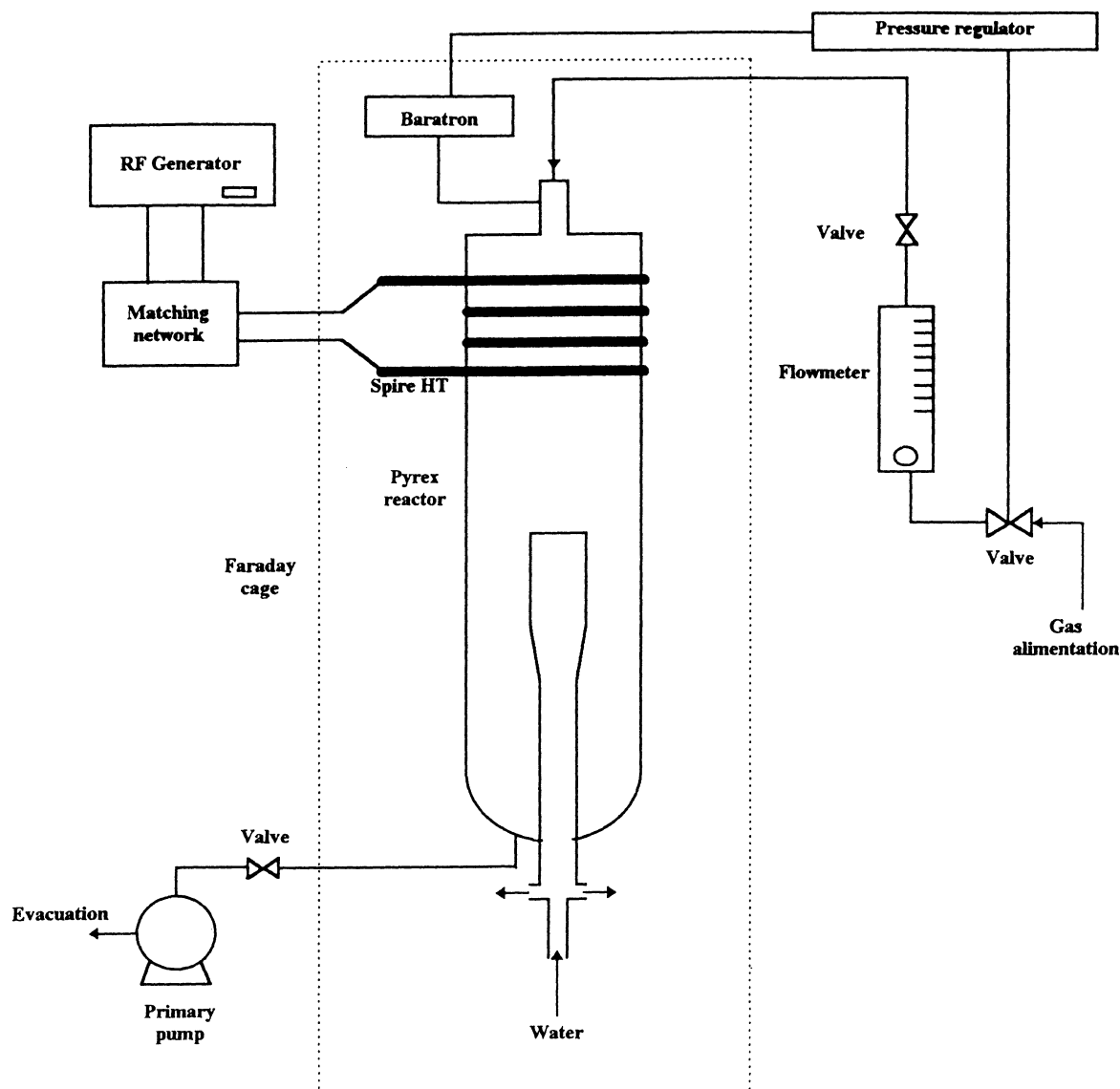


Figure 1 : General sketch of the device

A loss of mass of the solid in given conditions means that a part of the target is transformed into volatile species which are blown away with the flowing gas. Qualitative analysis was performed by means of specific Draeger test tubes positioned at the output of the reactor and revealed positive and

shows that CO_2 forms in the ultimate step of the degradation of 1,4-dihydroxybenzene at our conditions but could not be quantified. We also assume that water vapour forms to verify the mass balance, but no experimental argument is available. Hence, the most likely overall mechanism at this preliminary stage is given by the overall reaction :

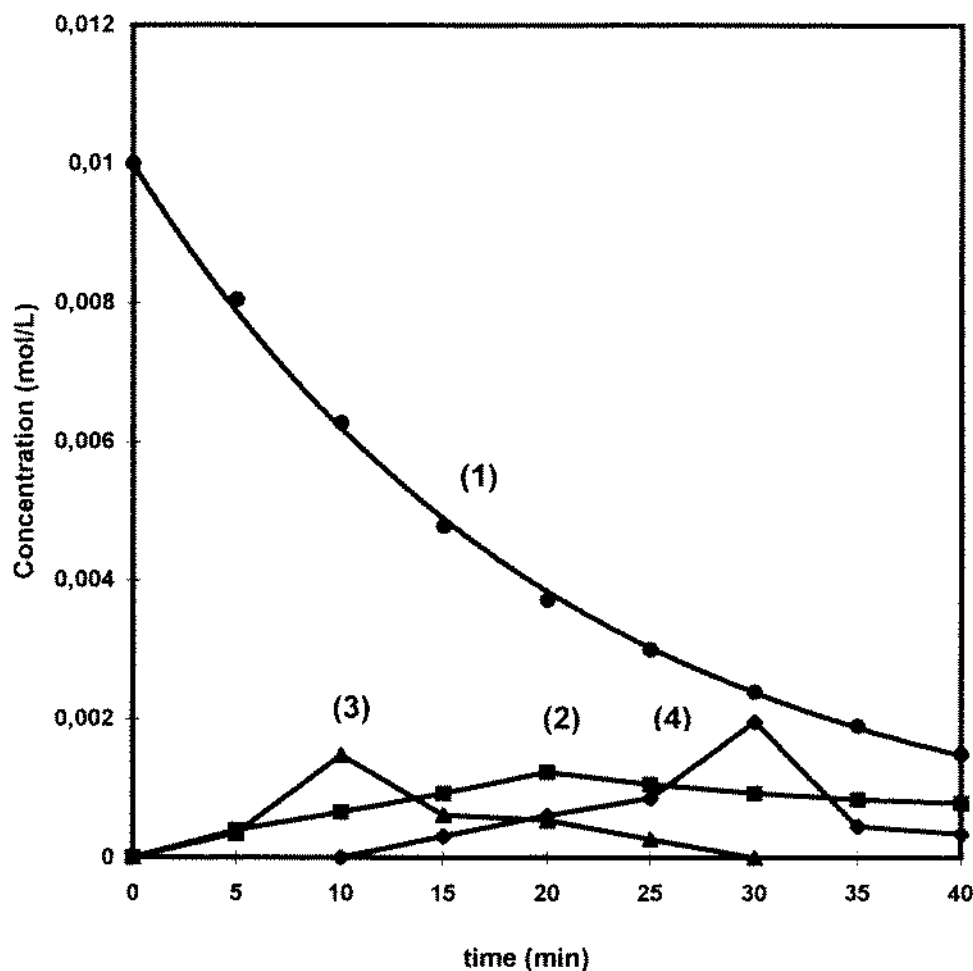
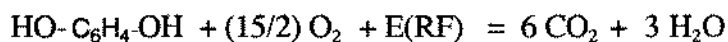


Figure 2 : Evolution with the treatment time t (min) of the mole numbers of the various intermediates (Plasma power density: $8.8 \cdot 10^5 \text{ W/mol}$).
 (1): 1,4 dihydroxybenzene; (2): 1,4 benzoquinone; (3): maleic acid; (4): oxalic acid.

In fact a more complex mechanism takes place, as suggested by a very light deposit of carbonaceous matter on the walls of the reactor, which also prevents verification of the carbon mass balance. Thus, the preceding reaction is only an overall result. Previous studies (17) relevant to the dissociation of CO_2 in an inductively coupled plasma showed the occurrence of the following

equilibrium : $\text{CO}_2 = \text{CO} + (1/2) \text{O}_2$. In the present study performed in oxygen, the equilibrium may be displaced in favour of carbon dioxide and any CO molecule should oxidise to CO_2 .

A sharper analysis of the degradation kinetics results from the use of electrochemical methods. For various exposures to the plasma, all shorter than one hour, the target was analyzed voltametrically which provided simultaneous information on the concentrations of both the oxidised form (Q) and the remaining species (H_2Q) from the values of the limiting currents. Starting from 10^{-2} moles of 1,4-dihydroxybenzene (H_2Q), we found that more than 50% of the substance was transformed within 20 minutes (Fig. 2). Also, the concentration of H_2Q decreases exponentially and tends to zero ($\text{C}(\text{H}_2\text{Q})_\infty = 0$) as the exposure time t to the plasma increases. Assuming a first order kinetics for the hydroquinone decay (i.e., $d\text{C}(\text{H}_2\text{Q})/dt = -k\text{C}(\text{H}_2\text{Q})$), then the integrated function $\text{Ln} [\text{C}(\text{H}_2\text{Q})_t / \text{C}^0(\text{H}_2\text{Q})] = -kt$ should be a linear function of the treatment time. The assumption is experimentally verified, and the line has a slope $k = 8 \cdot 10^{-4} \text{ s}^{-1}$. Such a feature agrees with a first-order mechanism with respect to H_2Q .

Hence the kinetic law may be written as:

$$v = -dC/dt = k.C(\text{solid}).C^n(\text{O}_2) \text{ or } -dC/dt = k.C(\text{solid}).C^n(\text{O}^\circ).$$

Two questions then arise. The first one is relevant to the nature of the species responsible for the oxidation process, i.e., O_2 or O° . The presence of O° in the plasma phase and the high value of the associated oxidation-reduction potentiel are serious arguments in favour of the occurrence of O° as the main reagent in the oxidation process. However the population of oxygen atoms is less than 10% of the gas species as mentioned (12).

The second question is related to the order of the reaction, that is with the value of n . The reaction is 1st order if $n = 0$ and pseudo 1st order if the oxygen concentration is constant, that is if the species is in large excess, which is verified at the experimental conditions for O_2 but not for O° . Important changes in the pressure might provide arguments to answer. An increase in the pressure should increase the kinetic rate, if we assume that the kinetic mechanism involves molecular oxygen ; correlatively, a decrease in the pressure should induce slower kinetics. If we consider now that the oxygen atoms are concerned, the rate should not be affected by an increase in the pressure because the density of O atoms is low and remains constant (12) for $p > 210 \text{ Pa}$. Also, a decrease in the pressure induces an increase in the population of oxygen atoms, and should consequently lead to an increased kinetic rate.

It is thus actually difficult to decide between these opposite arguments because neither an increase nor a decrease in the gas pressure can provide clear cut arguments to precise the reaction mechanism and to choose between a 1st order and a pseudo 1st order process. We must also remember that an increase in the pressure induces drastic changes in the characteristics of the plasma in favour of a thermal character : the treatment conditions should thus be completely modified, and any conclusion should be risky.

The influence of the applied electric power is now considered. The investigation is limited to the range 60 - 120 W because the kinetics rate increases with P , and it becomes difficult to get reliable results for standard 20 min treatments. As illustrated by Fig. 3 (curve 1), an increase in the applied

electric power induces a linear increase of the conversion ratio of 1,4-dihydroxybenzene (i.e., the mole ratio of transformed H_2Q moles / number of initial H_2Q moles). In the same conditions, the ratio of the 1,4-benzoquinone moles formed / starting number of H_2Q moles (Fig. 3, curve 2) presents a maximum at $P=80$ W, which confirms that 1,4-benzoquinone is again an intermediate. A similar feature is reported by Tezuka et al. (11) in their study of the oxidation of benzene in an O_2 plasma. This feature also confirms that an increase in the feeding power leads to faster reactions, as already observed for metal treatments (12).

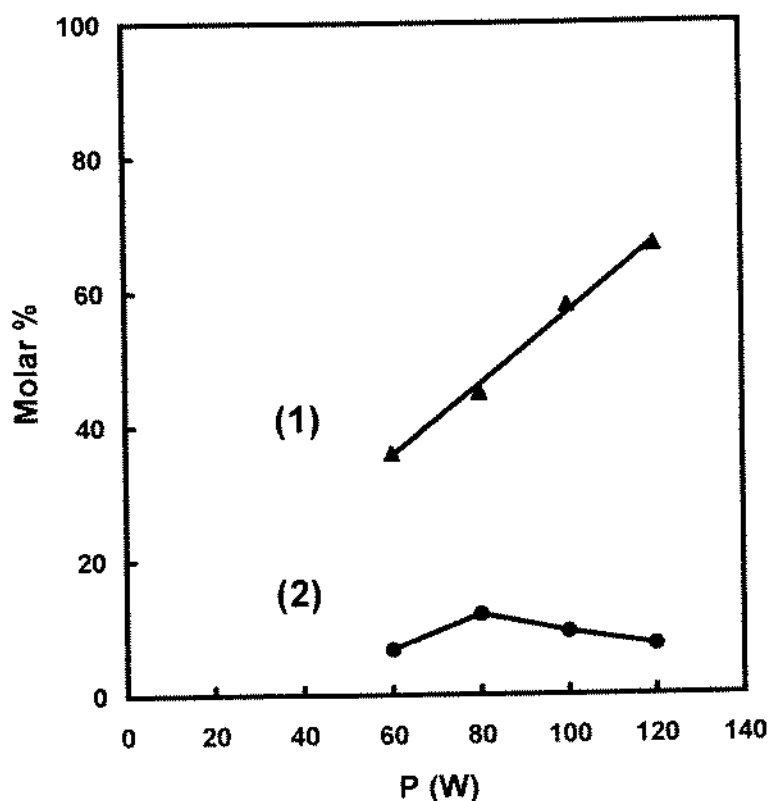
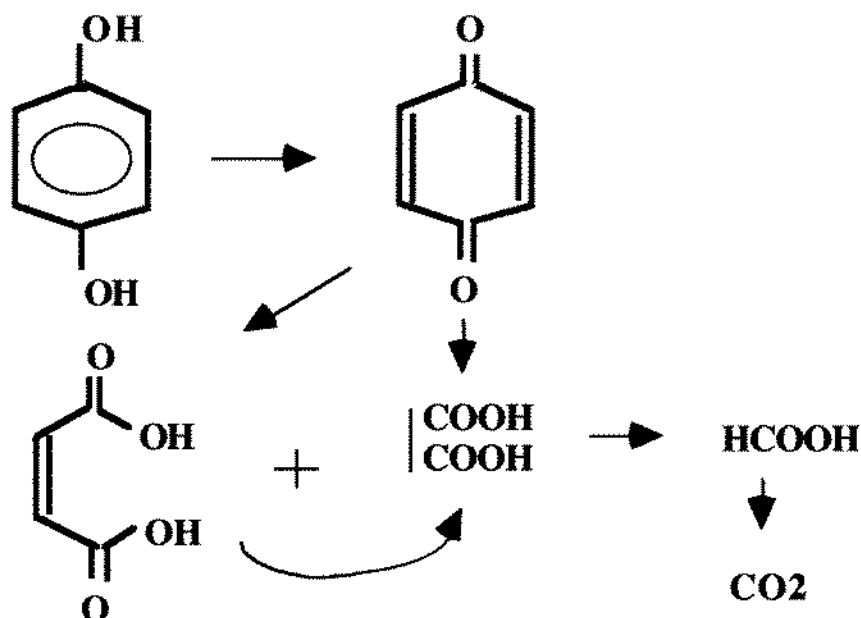


Figure 3 : Influence of the injected power on the oxidation yield of 1,4 dihydroxybenzene in an oxygen plasma ($p = 210$ Pa; $d = 20$ cm; $t = 20$ min). Curve (1) corresponds to the dihydroxybenzene mole ratio (transformed / starting) and curve (2) is relevant to the benzoquinone mole ratio (formed benzoquinone / starting dihydroxybenzene) .

These results show that an organic powder oxidises when exposed to a RF oxygen plasma at reduced pressure and at a temperature close to the ambient, which prevents the compound from sublimating. Hence, we have the use of a new tool to study the oxidation reactions of organics without the need of any solvent. We can foresee large forthcoming applications in the field of ageing studies of powdered chemicals under particular working conditions which must be precised, and we selected "smooth" conditions for the present study.

The concentration of the formed quinone changes with the exposure time and presents a maximum. Also, the sum of the concentrations $C(\text{hydroquinone}) + C(\text{quinone})$ which should keep constant in the case of a simple mechanism, decreases as t increases. This suggests that a more

complex mechanism governs the degradation of hydroquinone. For example, the transformation of hydroquinone to quinone may be followed by the subsequent degradation of quinone to acids and ultimately to volatile products (e.g., formic or carbonic acid, $\text{CO}_2 + \text{H}_2\text{O}$) as summarized by the following scheme:

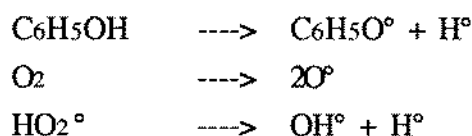


The occurrence of acids was detected from the pH changes of the solutions prepared from the dissolved target. Oxalic acid was first identified by GC : its concentration presents a maximum as the treatment time increases, which indicates that $(\text{COOH})_2$ is also an intermediate in the general oxidation scheme. Also, its maximum concentration remains limited to a few percent, which prevents the carbon balance to be verified. This suggest the additional formation of other intermediates, e.g., maleic or fumaric acids, the formation of which should agree with published (18) oxidation schemes. The formation of maleic acid was actually verified by GC, and the relevant concentration presents a maximum, which confirms its occurrence as an intermediate. The degrading evolution of maleic and oxalic acids by means of an oxygen plasma treatment was examined and discussed elsewhere (19)

This scheme agrees with the experimental results and with the literature. In their study in aqueous solution of the degradation of phenol by UV radiation, hydrogen peroxyde and oxygen, Schenck and Frimmel (18) consider that OH^\bullet formed by irradiation of H_2O_2 is responsible for the cleavage of benzoquinone to maleic and oxalic acids, and to the further oxidation of oxalic acid to formic acid and to carbon dioxide due to its high oxidation potential. However they were unable to detect 1,4-benzoquinone. In our experiments which directly involve no water, the occurrence of OH^\bullet as the main oxidizing agent does not hold, but that of the O^\bullet atoms is much more likely. Also we consider in our scheme the probable occurrence of formic acid for homogeneity reasons: this product was not detected since it was probably blown away with the oxygen flow as a volatile compound.

According to the early work by Norrish and Taylor (21), gas phase oxidation of benzene by oxygen proceeds via dihydroxybenzene and hydroquinone; hydroquinone is also said to react with oxygen to form maleic acid and acetylene. In our experiments we have no information about volatile compounds, and in particular about acetylene. Acetylene was not detected in our case as a volatile compound, because it might be completely oxidised at our plasma conditions.

Our kinetic scheme only signifies that the major steps of the oxidation process induced by the electric discharge are taken into account. Extra informations are hardly deduced from our experimental results. In particular the physical influence of the discharge on the initiating step of the reaction (i.e., the transformation of diphenol to quinone) remains hypothetical. However, we can rapidly examine published mechanisms to see whether they hold or not in our case. In supercritical water (22) phenol oxidation is claimed to involve the occurrence of the phenoxy radical resulting from unimolecular initiation steps:



Also, the formation of the benzosemiquinone radical $\text{HO.C}_6\text{H}_4.\text{O}^\bullet$ was shown long ago (23) from the radiolysis study of aqueous solutions of dihydroxybenzene (or hydroquinone). This radical is also involved in the radical ozonation of coumaric acid and relevant molecules (i.e., 4-hydroxybenzaldehyde) in aqueous solutions (24), as well as in the electrochemical oxidation mechanism of dihydroxybenzene. Hence the examined literature suggests that, in the oxygen plasma phase as in solutions, dihydroxybenzene is oxidized to benzoquinone via two rapid steps involving the semiquinone radical.

CONCLUSIONS

Exposure of 1,4 dihydroxybenzene pellets to a RF oxygen plasma leads to several oxidation products within few minutes of treatment. In our selected "smooth" conditions, 10 mmol of the starting solid oxidises to CO_2 within 1 hour according to a pseudo-first order reaction (half-time reaction around 20 min). Several intermediates are identified, such as the associated quinone, maleic/fumaric and oxalic acids. The main steps of the oxidation mechanism are proposed on the basis of pseudo first order reactions and the rate constants of the disappearance of 1,4-dihydroxybenzene is given. An initiation step involving the $\text{O}(^3\text{P})$ atoms generated by the electric discharge and the occurrence of a benzosemiquinone radical are assumed in agreement with published studies.

The presented work confirms the oxidising properties of an oxygen plasma, which were evidenced on organic liquids (9) and solids. This treatment is performed on organic powders and its efficiency suggests that the technique can be successfully used for ageing studies of powdered organic raw materials.

LITERATURE CITED

- [1] F. Cacace, *Acc.chem. Res.* **1988**, 21,215-222.
- [2] M.T. Bowers, *Gas Phase Chemistry*, Academic Press, New-York, **1979**
- [3] T.J. Mason, P.J. Lorimer; *Sonochemistry:Theory, Applications and Uses of Ultrasound in Chemistry*, Wiley, New-York, **1988**
- [4] H. Boenig, *Plasma Chemistry; Fundamentals and Applications*, Wiley, New-York **1988**
- [5] E. Pfender, *Pure Appl. Chem.* **1985** 57,1179
- [6] H. Holzschuh, H. Suhr, *Appl. phys A*, **1990**, 51, 486
- [7] L.L. Miller, A.B. Szabo, *J. Org. Chem.* **1979**, 44, 1670
- [8] Y.S. So, L.L. Miller. *J. Amer. Chem. Soc.* **1980**,102, 7119 and 103, 4209
- [9] P. Patino, M. Roperio, D. Iacocca, *Plasma Chem. Plasma Process.*, **1996**,4, 563
- [10] P. Patino, F.E. Hernandez, S. Rondon, *Plasma Chem. Plasma Process.*, **1995**,2, 159
- [11] M. Tezuka, Y. Yajima, *Plasma Chem. Plasma Process*, **1996**, 16, 329-340
- [12] N. Bellakhal, K. Draou, B. Chéron, J.L. Brisset; *Mat. Sci. Engin. B*, **1996**, 41, 206.
- [13] M. Langeron, F. Prévôt, S. Cavvadias, J. Amouroux; *Proc. ISPC-11* (Loughborough, U.K., **1993**), 639.
- [14] J.L. Brisset; *J. Appl.Electrochem.* **1997**, 27, 179
- [15] R. Weisbeck, D. Hüllstrung; *Chem. Ing. Techn.* **1970**, 42, 1302.
- [16] E. Inous, *J. Electrochem. Soc. Jap.* **1955**, 23, 18
- [17] A. Doubla, J.L. Brisset; *Pol. J. Appl. Chem.* **1996**, XL, 323
- [18] C.K. Schenk, F.H. Frimmel; *Wat. Res.* **1995**, 29, 2346
- [19] N. Bellakhal, J.L. Brisset, *Pol. J. Appl. Chem.*, submitted to publication.
- [20] J.P. Hoare, *Standard Potentials in Aqueous Solution*, A.J. Bard, R. Parsons, J. Jordan Ed.; M. Dekker, New York, **1985**, 49-66.
- [21] R.G.W. Norrish, G.W. Taylor; *Proc. R. Soc.* **1956**, A224, 160
- [22] S. Gopalan, P.E. Savage; *J. Phys.Chem.*, **1994**, 98, 12646
- [23] G.E. Adams, B.D. Michael; *Trans. Faraday Soc.*, **1967**, 63, 1171
- [24] R. Andreozzi, V. Caprio, M. G. D'Amore, A. Insola; *Wat. Res.*, **1995**, 29, 1.