GLIDING ARC TREATMENT OF AQUEOUS SOLUTIONS NEAR ATMOSPHERIC PRESSURE

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Abstract

The treatment of aqueous solutions by a gliging arc operated in air induces drastic changes on the solutes which are examined from the chemical point of view. We report here on the strong acid and oxidizing effects observed within one hour treatment on millimolar solutions. Advantages of such effects can be taken in the field of depollution and waste treatment.

Introduction

The use of a gliding arc (i.e., a "glidarc") for the treatment of gases was already investigated at the Orleans University and appeared to be an interesting possibility [1-4]. We wished to develop the applications of this new device, and we report here on the treatment of aqueous solutions. In order to settle our knowledge of the chemical properties of such a plasma, we exposed an aqueous solution to an air glidarc and we followed the composition of the liquid phase as a function of the treatment duration. From this fundamental approach, we expect useful informations on the oxidizing properties of this plasma, that may be obviously interesting to explain the treatment of gases and solids. We report here both on the acid-base properties and on the oxidation-reduction effects of the plasma treatment realized by a glidarc in natural air.

Experimental

The A.C. glidarc device is described elsewhere [1]. The stainless steel electrodes are disposed at a distance of 2 mm and at 22 mm from the surface of the aqueous target. The air flow is controlled at 5.25 $L.min^{-1}$ for the temperature and evaporation measurements and at 3.15 $L.min^{-1}$ for the other experiments which are performed with an electrode-to-target distance of 30 mm. The standard electric working conditions are: I = 100 mA: U= 10 kV.

All chemicals are commercially available and used without purification.

Potassium picrate is prepared at the laboratory and analysed satisfactorily.

Acidity measurements are performed with the help of a conventional pH-meter device fitted with a standard glass electrode; potentiometric measurements are also conventionally obtained by means of of a set of Pt/SCE electrodes. The concentrations of the coloured solutes are determined spectrophotometrically at their absorption peaks.

Results and Discussion

Physical effects

We report here the results of treatments of aqueous solutions by an air glidarc. The air flow is fixed value as well as the other experimental conditions (e.g., the current intensity, the voltage fall between the electrodes, the electrode gap,...) Under these conditions the plasma is expected to be stabilized and allow a standard treatment of the target.

First of all two efffects are observed: evaporation of the solvent and a noticeable rise in the temperature of the liquid. The evaporation is easily quantified by weighting the target (Fig. 1). These data enable us to operate at constant weight, by adding the missing quantity of solvent and get correct concentrations of the solutes. The temperature of the target rises but remains limited to a few tens of degrees, and never exceeds 50°C (Fig. 2).

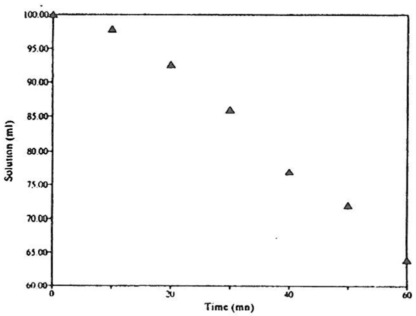

Fig. 1- Evaporation with time of the water target treated for one hour. (air flow: 5.25 L.min^{-1}; distance from the target to the electrodes: 22 mm)

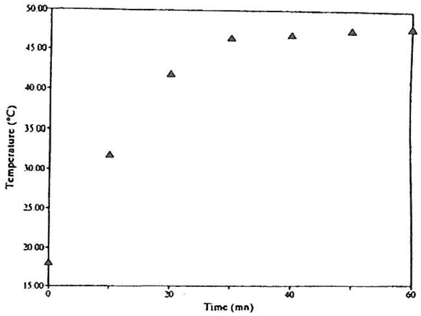

Fig. 2- Temperature evolution of the water target treated for one hour. (air flow: 5.25 L.min^{-1}; distance from the target to the electrodes: 22 mm)

Chemical effects

a- acid effect

Exposure to the plasma of soda solutions induce a pH fall of more than seven units (Fig. 3), and the pH *vs.* time plots look like classical acid-base titration curves. The equivalent points are obtained for various exposure times t_{eq} which are linearly related to the starting concentration of soda (Fig. 4). In addition, the log plot pH*vs* log(1 - t/t_{eq}) is satisfatorily linear, in agreement with a coulometric titration.This suggests that the plasma generated gaseous species drift into the liquid phase and neutralize the hydroxy anions, exhibiting by the way the properties of a strong acid.

Besides, the shape of the titration curves retains attention, since the pH fall tends to a pseudo-limit observed after the equivalent point. This "limit" is common to all the plots and its constant value is close to pH = 3.5. Such a feature suggests that a Nitrite/ Nitrous acid buffer [$pK_a(HNO_2/NO_2^-) = 3.29$] can be involved in the titration reaction.

The occurrence of nitrites is directly related to oxidation phenomena, involving nitrogen from air as the starting material.

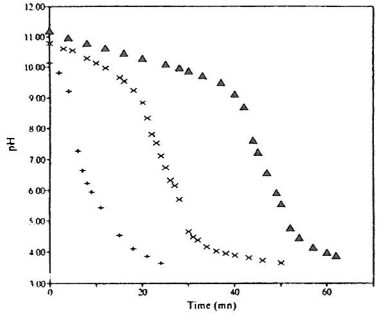

Fig. 3- Acidity fall of 50 mL of (2.5 10^{-3} M[triangles]; 1.25 10^{-3} M [x] and 0.5 10^{-3} M [+]) soda solution as a function of the time exposure (minutes) to the glidarc.

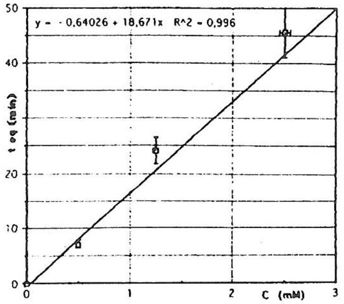

Fig. 4- Correlation between the time exposure (t_{eq}, min.) to reach neutrality and the soda solution concentration (C, millimol L^{-1}). Volume: 50 mL

b- oxidizing effects

The oxidizing efffects of the air glidarc treatment are evidenced on the basis of several examples selected among inorganic or organic solutes in aqueous media.

We first confirm by means of specific tests the occurrence of nitrites and nitrates which appear as the matching ions to the protons to fulfill the charge balance in the solution, as already observed in the case of a corona discharge in humid air [5]. The study of the kinetic evolution of the concentrations is under progress.

A Mohr salt (50 mL of 10^{-4} M solution) treated by the air glidarc was followed potentiometrically at the equilibrium, as shown on Fig. 5. The plot E(mV/ SCE) *vs.* time (minutes) is equivalent to a classical potentiometric titration curve. Before the equivalent point the solution potential depends on the activity ratio $a(Fe^{3+})/a(Fe^{2+})$. Assuming that the Fe^{3+} concentration is proportional to the time exposure $C(Fe^{3+}) = kt$, then the solution potential obeys a bilogarithmic kinetic law: $E = cst + (RT/nF) \ln [kt/(1-kt)]$: the inflexion point ($E^* = 500$ mV/SCE; $t^* = 1518$ min) leads to the k value ($2kt^* = 1$; hence $k = 0.36\ 10^{-3}$ mol.min^{-1}) and verifies the standard potential of the iron system. The discrepancy (i.e., 13 mV) is very limited and attributed to the ionic strength effect and the junction potentials. In addition the log plot (i.e., E *vs.* log $kt/(1- kt)$) is satisfactorily linear with the correct slope for $t<t^*$; however for $2t^*>t>t^*$ the slope is too high for a mere one-electron process and the oxidation mechanism is actually more complicated.

After the equivalent point ($t>2t^*$) the solution potential tends to a limit value close to 800 mV/SCE. This feature may be related to: i) the pH change of the solution if the oxidizing system is pH dependant and ii) the limited solubility of the oxidizer related to the poor stability of activated species.

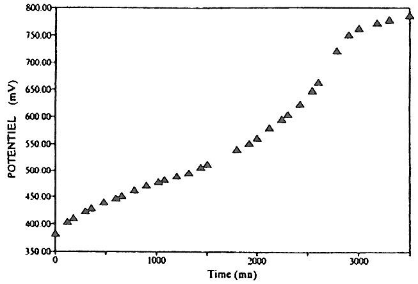

Fig. 5. Potentiometric evolution of an aqueous solution of Fe^{2+}treated by an air glidarc.

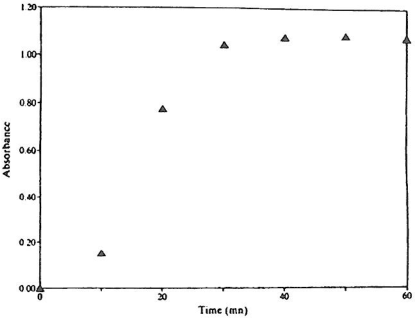

Fig. 6. Evolution of the absorbance of the ferricyanide when a ferrocynaide solution is treated by by an air glidarc

Aqueous solutions of (10^{-4} M) ferrocyanide or iodide (10^{-4} M) are also oxidized into ferricyanide and iodine repectively and the absorbance of the solutions is recorded as a function of the time exposure. Fig. 6 is relevant to the ferrocyanide solution and Fig. 7 to the iodide solution. Since the absorbance is directly proportional to the concentration, we can follow the concentrations of the oxidized solutes $Fe(CN)_6^{3-}$ and I_2. The relevant plots are very similar: after a delay of a few minutes, the concentrations of the oxidized species increase linearly with the treatment time and reach limit values after 30-40 minutes corresponding to the completed reactions.

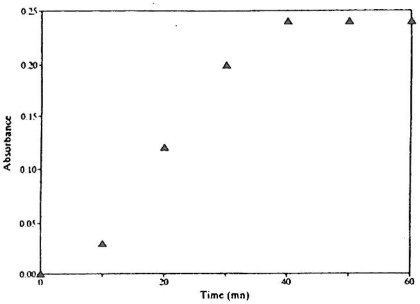

Fig. 7. Air glidarc oxidation of a (10-$^{-4}$M) iodide aqueous solution: variation of the absorbance as a function of the time exposure

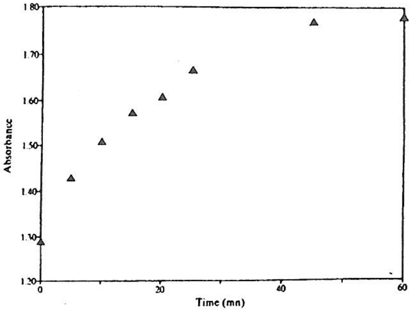

Fig.8. Air glidarc treatment of a (5.10^{-4} M) aqueous solution of phenol C_6H_5OH (pH:7.6; 100 mL; Air Flow: 5.25 L.min-1).Variations of the absorbance with the time exposure.

Phenol solutions were also exposed to the plasma and the absorbance A measured at the absorption peak of the molecule. Absorbance at 220 nm increases with the time exposure (Fig. 8) and a pseudo first order kinetic law can be deduced from the recorded experimental values. The plot ln $|A_\infty - A|$ vs. t is linear and its slope gives the kinetic constant k (k= 0.014 M min^{-1}). At this juncture, we may point out that pseudo first order kinetics were also observed for the degradation of phenate by the neutrals of an A.C.corona discharge in humid air [6].

A tentative interpretation

All the reported results are consequent with the occurence of a highly oxidizing species which is formed in the discharge and drift into the solution where they react with the convenient reducer to yield the oxidized matching form. In some cases the reaction is limited to the formation of one oxidized species (e.g., Fe^{2+} --> Fe^{3+}) but it can occasionnally go ahead and undergo a second oxidation step (e.g., N(0) --> N(III) ---> N(V) or the destruction of phenol).

The nature of this parent oxidizer remains conjectural, but one can point out that no particular species results from its reduction. So that one can consider as a basic but serious working assumption the occurrence of a radical such as HO° or HO$_2$°, which are well known as highly active reagents in water radiolysis for instance. The standard oxidation potential of the OH°/OH$^-$ system is 2.8 V/NHE, superior by about one volt to that of the HO_2°, H^+ / H_2O_2 system (i.e., 1.7 V/NHE). Both values are high enough to let OH° or HO2° oxidize water (E° (H_2O/O_2) = 1.23 V/NHE) with the matching production of protons. The associate reducers are then H_2O_2 and O_2 which are species usually formed in a discharge in humid air.

In addition, some attention must be paid to the quantitative kinetic aspect. The formation of the oxidizing species created (i.e., OH° or HO_2°) is a direct consequence of the occurrence of an electric arc. Hence the number of the species formed must be directly related to the quantity of electricity involved in the discharge, although this quantity is difficult to determine in the case of an electric arc.

The examples herein presented are relevant to two different kinetic behaviours. The concentrations of iodide and ferrocyanide vary linearly with the time exposure after a delay, and the oxidation products (i.e., iodine and ferricyanide) are connected with a one electron oxidation step. At the opposite the oxidation of phenol leads to the total destruction of the molecule by a sequence of reactions including the ring opening and the formation of diacid intermediates.

Conclusion

The acidifying and oxidizing effects of the humid air glidarc on aqueous solutions are evidenced on various examples selected among organics and inorganics. The kinetic laws depend on the oxidation-reduction system examined, but in the case of processes involving multistep reactions such as the complete oxidation of phenol, an overall pseudo first order kinetic law is observed which may be related to the diffusion of the active species in the solution.

A particular application of the reported results may be found in the removal of phenols from wastes waters, and more generally in the oxidative destruction of priority pollutants.

Literature cited

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