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ACID-BASE REACTIONS INDUCED BY A PLASMA PHASE ON LIQUID TARGETS : BRONSTED ACIDITY AND OXO SYNTHESIS⁽¹⁾

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Résumé - Les interactions cible liquide-plasma (produit par décharge couronne pointe-plan continue à pression atmosphérique) sont examinées en termes de réactivité acide-base aux sens de Bronsted et de Lewis. Le traitement de solutions aqueuses par les neutres activés d'un plasma d'air ou de NH₃ accroît l'acidité de la cible: pour un plasma d'air, ΔpH est une fonction linéaire de la quantité d'électricité mise en jeu par la décharge. Un modèle d'interaction très élémentaire implique la vapeur d'eau et souligne le rôle déterminant de l'oxygène singulet. Des applications résultantes, d'ordre analytique, permettent de préciser les caractéristiques géométriques de la surface traitée par les neutres activés en fonction des paramètres de fonctionnement de la décharge et de l'acidité initiale de la cible. Le traitement d'oléfines liquides par une décharge couronne dans CO + H₂ conduit à la formation de dérivés carbonylés et illustre les propriétés d'acide-base de Lewis du plasma considéré.

Abstract- The interactions between liquid targets and plasmas provided by a d.c. point-to-plane corona device operated under p = 1 atm. are considered in terms of both Bronsted and Lewis acid-base reactions. The treatments of aqueous solutions by the chargeless species of air or NH₃ plasmas increase the Bronsted acidity of the target, and for an air plasma, the pH decrease is a linear function of the quantity of electricity involved in the discharge. The simplified model proposed for these water-plasma interactions involves water vapour and singlet oxygen. Analytical applications are also developed to determine the area treated by the activated neutrals, with respect to the operating conditions. The treatment of liquid olefins by a CO + H₂ plasma under corona conditions illustrates the Lewis acid-base character of the relevant plasma, and leads to the formation of carbonylated compounds.

1- INTRODUCTION

The undertaken study aims to rationalize the plasma-surface interactions. It is focused on one of the large families of chemical reactions: the acid-base reactions.

When limited to the proton exchange reactions, i.e., to the Bronsted acidity, the acid-base reactions are well defined and known if they take place in a solvent phase. In the gas phase, the gas acidity and basicity are similarly quantified by the Gibbs energy of the proton exchange reaction. The gas acidity or basicity of a number of compounds are determined; this makes them able to be classified by means of the proton affinity (PA)

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which is an approached value of the Gibbs energy. The literature PA values are of definite fundamental interest, but they cannot be directly correlated to the thousands of data of acidity constants available for aqueous or non-aqueous solutions: their practical use as a predicting tool for the plasma/surface interactions remains thus limited since water molecules are adsorbed at the surface of most solids exposed to the atmospheric environment.

For the sake of simplicity we selected liquids as the targets exposed to the plasma since the acidity can be defined and measured in particular solvents (e.g., water) and the d.c. point-to-plane corona discharge as the plasma source, since it can be operated at atmospheric pressure and close to the ambient temperature and thus appears as a simplified model of the thermal plasmas. In addition, a drastic increase of the Bronsted acidity of water (pH falls from 7.5 to 4.3) has just been pointed out by authors /1/ dealing with underwater plasma arc cutting, and this illustrates the practical importance of this acidifying effect.

The corona discharge which was thoroughly studied by physicists /2/ takes place between two unsymmetrical electrodes (e.g., a point and a plane electrodes) when the point electrode is raised to the convenient (positive or negative) high voltage. When the discharge burns ions and chargeless species are generated in the neighbourhood of the point electrode. The ions migrate to the low field electrode and follow the electric field lines in the electrode gap; the neutral species are carried away by the electric wind and drift along the axis of the point electrode /3/. Both ions and neutrals are in their fundamental state or raised to some excited state, which confers to them an enhanced reactivity.

The first step to study the chemical properties of the plasma generated species is to separate the ion and the neutral fluxes. We could then focus on the chemical properties of the chargeless species alone and we have not to consider the oxidation-reduction reactions occurring at the electrodes nor the chemical effects of the ions which are developed in a matching paper /4/.

The separation is realized by several methods. For this study of the Bronsted acidity of aqueous solutions (i.e., the proton concentration changes in the target) we used as the plane electrode a grid /5/ which acts as an ion collector and is transparent to the chargeless species (Fig. 1a). For the oxo synthesis we preferred a particular lay-out of the electrodes (Fig. 1b): the point and the plane electrodes are parallel, which makes perpendicular the fluxes of the ions and the neutrals.

2- EXPERIMENTAL SECTION

The general device is shown in Fig.1. The liquid target is placed in a beaker under the grid (Fig.1a) or under the point electrode (Fig.1b). In all cases the liquid surface is perpendicular to the axis of the point electrode.

The general procedure was given /6-10/. The pH measurements /6,7/ are performed on small volumes (i.e., 7.5 mL) of dilute NaOH solutions ($3.5 \cdot 10^{-4} \text{M}$) of stabilized ionic strength ($\text{KCl } 10^{-2} \text{M}$) after vigorous stirring. For the analytical developments a commercial indicator (Bromothymol blue, BBT) is dissolved in alkaline aqueous solutions and trapped in a polymethylacrylamide gel /7,8/. For most experiments, the point electrode is raised to the negative HV.

For the oxo synthesis /9,10/ the 1-hexene purchased from Aldrich is used without purification and the reaction products are analyzed by FTIR spectrometry and GC. The CO input in the reactor is made through the hollow point electrode raised to the positive HV.

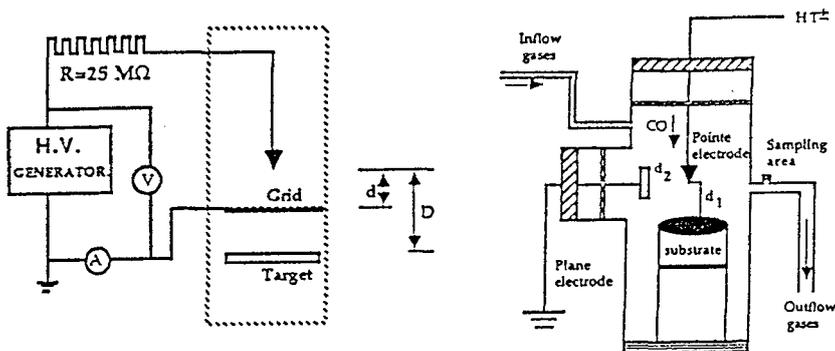


Fig 1a.- Scheme of the reactor. The point electrode is raised to the HV and the grid is earthed.
 Fig 1b.- Experimental device for the hydroformylation of 1-hexene (oxo synthesis) by $\text{CO} + \text{H}_2$.

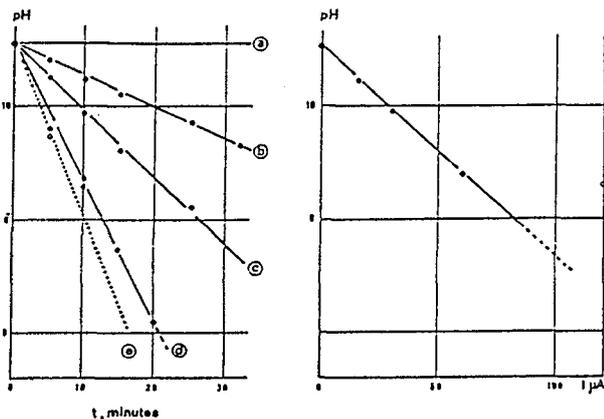


Figure 2.- Plots of pH vs. exposure time for various intensities of the discharge

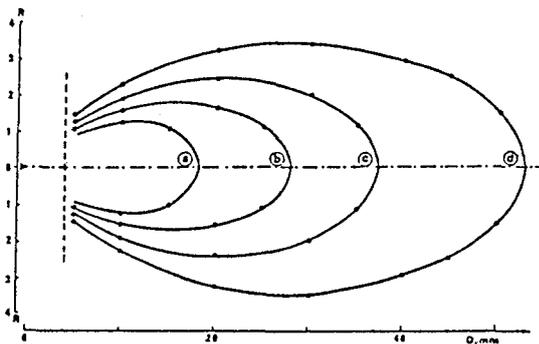


Figure 3.- Variations of the acid spot diameter vs. the point-to-target distance. R (mm) = $\phi/2$ is plotted against D (mm) for various intensities I (μA) = 60 (a); 90 (b); 120 (c); 170 (d); electrode gap $d = 4$ mm.

3- RESULTS AND DISCUSSION ON THE BRONSTED ACIDITY

Preliminary results /11/ gave evidence of an acid change of the aqueous solution under exposure to the neutral flux of an air plasma (e.g., the pH of a KCl (10^{-4} M) solution was lowered from 6.4 to a value close to 2.2). A similar treatment of aqueous solutions by the neutrals of a NH_3 plasma or the use of an anhydrous protic target (e.g., acetic anhydride and acid) treated by an air plasma led to a noticeable enhancement of the acidity of the targets. These experiments demonstrate that solvated protons are created in the solvent by the discharge. Since the discharge takes place in the gas phase among unsolvated species we must assume that the solvent vapour takes a determinant place in the relevant mechanism. Complementary qualitative tests for NO_2^- and NO_3^- ions (i.e. the diphenylamine test, the Reichardt reaction with brucine or the Griess reaction) were found positive for both polarities of the discharge in water saturated air.

We quantified /6/ the acidity changes of an aqueous solution by measuring the pH variations of soda solution exposed to the neutral flux of a (negative) corona discharge in air and fixed experimental conditions (e.g., electrode gap: 17.4 mm; stabilized intensity, resp. 0- 15- 30- 60- 120 μA and constant point-to-target distance). After vigorous stirring to homogenize the solution, the pH stabilizes at values which are in linear correlation with the exposure time. Moreover, the pH variations for a given exposure time are a linear function of the current intensity (Fig.2). This result gives evidence that the acidification phenomenon is directly related to the quantity of electricity involved by the discharge.

A preliminary model for the acidification of the target was then proposed /6/. It assumes an equilibrium between the solvated protons in the gas phase (gas clusters) and solvated protons in the target (solution clusters) which may be characterized by the Henry constant. It is then easy to integrate the variations of the solvated proton concentration in the solution and we get for a given intensity the variation law :

$$\text{pH}_0 - \text{pH} = 2.303 k (t - t_0)$$

where k is the kinetic constant which depends on the current intensity.

A puzzling question is relevant to the nature of the chargeless activated species which are responsible for the formation of the clusterized protons in the gas phase. The most probable species have been listed /12-14/ but additional informations can be given. Since the discharge is operated in air, of which molecular oxygen and nitrogen are the major components, these species appear as the most likely to be considered for the origin of the CAS, if the reaction products formed by the oxidation-reduction reaction at the point electrode are not taken into account. To balance the relative influence of excited N_2 or O_2 a series of discharges were performed on standard aqueous soda solutions of acid-base indicator (BBT) with or without a quencher of singlet oxygen added (e.g. NaN_3). For an air discharge, the pH decreases by 2.3 units when NaN_3 is not present and only by 1.2 units in the other case. For an oxygen discharge, the pH decreases are respectively 3.2 and 0.5 pH units. It can be then concluded that excited nitrogen contributes to the acidification of the solution as well as singlet oxygen but at a lower extent. Although the complete set of reactions giving rise to the clusterized protons in the gas phase is still unknown, the prominent influence of singlet oxygen may be additionally related both to its well known reactivity as a Lewis acid and to its great ability to dilute in an aqueous solution.

4- APPLICATIONS TO ANALYSIS

Another technique was used to measure and visualize the acid effects induced by the

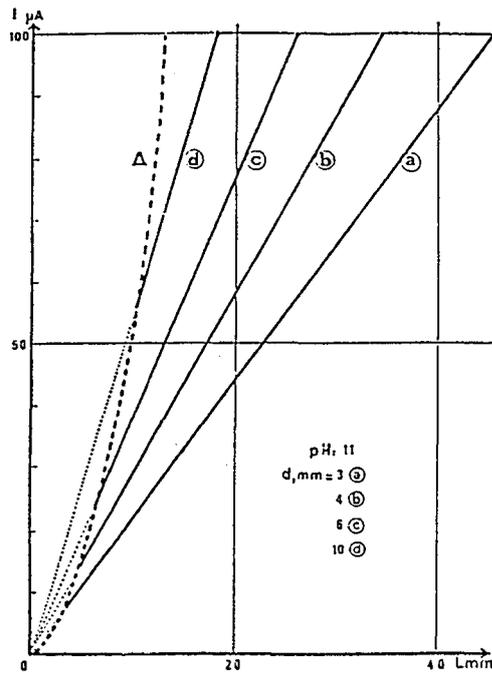


Fig. 4.- Observation threshold in air, L(mm), measured from the point, as a function of I (μA). the curves (a) to (d) are relevant to various electrode gaps, resp. 3 mm (a); 4 mm (b); 6 mm (c); 10 mm (d). The limiting curve Δ is defined from the gaps relevant to each straight line.

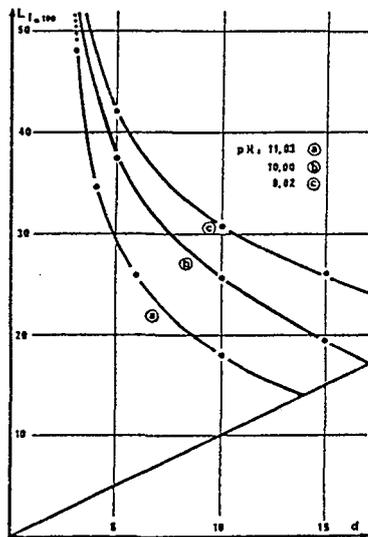


Fig. 5.- Observation threshold L(mm) in air for various electrode gaps and a fixed intensity $100 \mu A$. Acidity of the target, $pH = 11.03$ (a) ; 10.00 (b) ; 9.02 (c).

activated neutrals of an air discharge on an aqueous target. An alkaline solution of acid-base indicator was trapped in a layer of polymeric gel to limit evaporation, and subsequently exposed to the activated neutrals of the discharge. After a few minutes exposure a circular spot developed on the gel, along the axis of the point electrode, and the colour of the spot was that of the acid form of the indicator. It was then possible to estimate the diameter \emptyset of the spot and to relate it to various working parameters, since it reflects the spreading and fading of the neutral flux at the stabilized liquid surface.

This technique allowed us to study [7,8] the influence of the intensity, the voltage the electrode gap d or the exposure time which are gathered as "electric parameters", that of the point-to-target distance (or observation distance D) as the "geometrical parameter", and that of the initial acidity of the target or the acidity constant of the indicator as the "chemical parameters".

4.1) - The "electric parameters"

For a given configuration of the reactor (i.e., the gap d and the distance D), the diameter of the acid spot is an increasing function of the voltage, the intensity and the treatment time. As a first approximation due to the accuracy in the measure of \emptyset , one can consider that \emptyset is a linear function of the square root of both I and t , or of the square root of the quantity of electricity involved in the discharge, and this is consequent with the results already reported.

4.2) - The "geometric parameters"

For fixed values of the gap d , the intensity and the voltage, \emptyset presents a maximum as D increases and takes a value \emptyset_{\max} which depends on I , U , and t . Also, the particular value $\emptyset = 0$ is associated to a particular value of D , called the observation threshold L , since the chemical effects cannot be observed for higher values of D in the given conditions. Various plots of \emptyset vs. D for given values of U , I and gap are reported in the figure 3, which also illustrates an interesting feature: the values of \emptyset_{\max} and L are directly related to the intensity. We have then between the relevant values of \emptyset , L and I :

$$\emptyset_{\max} / \emptyset_{\max}' = L / L' = I / I'$$

Such relations may be used for predicting purposes of practical interest, since they allow to estimate the threshold for a given chemical treatment provided the intensity is known. The linear correlations between I and L for various gaps and initial acidities of the target are illustrated by figure 4.

4.3) - The "chemical parameters"

The described experiments were performed with the bromothymol blue as the standard indicator, but they could easily be reproduced with other indicators and similar conclusions resulted. However, the values of \emptyset_{\max} (and L) were different and depended on the selected indicator. For a given initial acidity pH_0 of the target and a standardized plasma treatment, the larger is the diameter of the acid spot the higher is the acidity constant pK_a of the indicator.

This result is easily understood if we remind that the color transition of an indicator takes roughly place (i.e., depending on the indicator) for $pH < pK_a - 1$. The color change which delimits the acid spot is then associated to the variations of the local acidity: $pH_0 - (pK_a - 1)$. The number of protons induced by the burning discharge in standard conditions (i.e., with controlled U , I and t values) is fixed and governed by the quantity of electricity It and probably by the electrolysis laws. The protons modify the pH of an homogeneous solution or lower the pH of a trapped gel solution at the impact area. Since the diffusion phenomena are limited in the gel, the diameter of the acid spot and the indicator strengths vary in opposite directions. In a similar way, the larger is the acid spot diameter relevant to a standard treatment and a given indicator, the closer to the pK_a is the initial pH of the target.

A consequence of these results appears in Fig.5 where the observation threshold

for fixed initial target acidities is plotted against the gap. Such a set of graphs is of an obvious interest both to check the correct experimental conditions for the discharge and to determine the maximum distance allowed to put a target in a standard corona treatment. This predicting argument is backed up by complementary experiments performed with a wire-to plane device which led to similar observations.

4.4) - Conclusions

The Bronsted acidity induced in a liquid target by the neutrals of an air plasma is then quantified and the parameters of determinant influence selected. This may be helpful to elucidate the pitting corrosion phenomena /15/ of metallic sheets observed under exposure to a point-to-plane corona discharge. For such treatments which result in the drastic destruction of the target, the chemical effect of both neutral and ion fluxes must be considered as well as the oxidation-reduction reactions occurring at the electrodes, but the relative influence of each kind of reaction remains to be specified.

5- APPLICATIONS TO THE LEWIS ACIDITY AND THE OXO SYNTHESIS.

The Lewis acidity which corresponds to the exchange of an unshared electron pair between an acceptor and a donor molecule can be also illustrated by the point-to-plane corona discharge. A good example /16/ is provided by the replacement of a nitrogen containing ligand (i.e., the N methylpyrazinium cation) by CO in the pentacyano (methylpyrazinium) ferrate(II) complex in aqueous solution. Under plasma conditions the exchange kinetics is realized in a few minutes while it takes several hours by simple bubbling of CO in the complex solution.

Another and more practical illustration results from the treatment of a liquid olefin by a CO + H₂ plasma /9,10/. The device used to filter the ions in this point-to-plane corona treatment is shown in Fig.1b and the reactor is characterized by two different gas inputs. CO is injected in the reactor through a hollow point and the hydrogen input is disposed on the side of the reactor, so that all the CO can be activated by the discharge.

Small volumes (i.e., 3.5 to 5.5 mL) of selected olefin (e.g., 1-hexene) are exposed for a few minutes to the flux of the neutrals produced in a point-to-plane corona discharge. The analysis of the resulting products gives evidence of the formation of alcohols and carbonylated compounds (aldehydes,...). The general unbalanced equation



must be completed by similar reactions which result from the occurring cracking reactions and the preliminary isomerizations of the double bond. This leads to a complex mixture of reaction products which are not yet all identified. The GC recordings and the IR spectra show that the quantities of products increase with the intensity and the treatment time or otherwise with the quantity of electricity involved in the discharge. In addition the gas ratio CO/H₂ has been optimized at 0.5 for the formation of the alcohols. The work is still in progress and we concentrate on a more accurate determination of the products and on improving the yields by testing new reactor device.

6 - CONCLUSION.

The presented study gives evidence that protons are generated when a point-to-plane corona discharge burns in a gas (air, ammonia or oxygen) saturated with a protic solvent vapour. With the help of the electric wind, the protons are able to drift in the liquid phase and acidify the target. The relevant pH decay was measured and is directly correlated to the quantity of electricity involved in the discharge. The presence of singlet oxygen quencher drastically limits the acidification process and this strongly suggests

that this particular excited species takes a prominent part in the associated mechanism. In addition, a series of tests involving gel trapped solutions are reported which allow to predict the area of the target treated by the neutrals of the discharge, which is of obvious practical interest.

The plasma-liquid interaction has also been examined on the example of the oxo synthesis. This investigation is of major industrial interest since the formation of alcohols and carbonylated organics results from a mere corona treatment of a liquid olefin in operating conditions close to the standard ones and without the use of catalyst.

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