



Disposal of spent tributylphosphate by gliding arc plasma

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Abstract

The gliding arc in humid air is a relevant source of free radicals and strongly oxidising species such as HO• (shown by emission spectroscopy), which are able to degrade organic wastes. This feature was used in a new process for mineralising spent tributylphosphate (TBP) which is an important waste from nuclear industry. The degradation kinetics is examined by monitoring the conversion of TBP into phosphoric acid in a batch reactor. The kinetics exhibits three steps and especially an overall zero-order linear step with a rate of 10 mmol h⁻¹ at the beginning of the treatment. This zero-order step agrees with a surface oxidation process. After a 13.7 h treatment, about 45% of the TBP is converted into inorganic phosphorus compounds, with phosphoric acid as the major product (63% of inorganic phosphorus compounds), and at least 19.5% is not degraded. Dibutylphosphoric acid (HDBP) was identified as the main by-product by a nuclear magnetic resonance technique, infrared spectroscopy and gas chromatography.

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1. Introduction

Tributylphosphate (TBP), is a widely used extraction solvent involved in nuclear fuel reprocessing, and particularly in the Purex process which is intended to recover uranium and plutonium from spent fuel. During the process TBP undergoes radiolytic and chemical ageing which fades its properties [1]. TBP is thus among the main spent solvents produced by the nuclear industry. Additionally, it is listed among the highly radioactive liquid wastes

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(HRLW) which must be mineralised before conditioning [1]. Several processes designed to mineralise radio-contaminated spent solvents are described elsewhere [2–4].

An original process to degrade TBP by means of a non-thermal plasma technique at atmospheric pressure is proposed in this paper. The available and operational non-thermal plasmas operated in conditions close to atmospheric pressure and room temperature, are corona and gliding arc discharges. We selected the gliding arc discharge method (“glidarc” device) because the working conditions make this device attractive both for industrial applications and/or for fundamental investigation.

The glidarc device is a very efficient and cheap source non thermal plasma. It is described elsewhere and exhibits a dual character of thermal and non-thermal plasma [5,6], so that its interactions with matter are those of quenched plasma. It thus presents an attractive feature both for scientists for modelling [7,8], and for industrials because it involves relatively high electric powers [5,6] compared with the corona discharge (in our case the power of the transformer is a few hundreds Watts). The interest then lies in the unusual chemical properties and enhanced reactivity of the heavy activated species (atoms, radicals and excited molecules) produced in the plasma.

The gliding arc was first successfully investigated for gas treatment [9–11]. More recently, we applied the humid air glidarc technique to the treatment of condensed matter. On exposing aqueous solutions, remarkable chemical properties could be evidenced in the condensed matter [12–14]: acidic and oxidising properties were observed and quantified in aqueous solution. Such properties are directly related to the composition of the plasma gas, which was investigated by molecular emission spectroscopy [7,8]. The presence of radicals ON^\bullet and HO^\bullet [8], and the molecular and atomic ions N_2^+ and O^+ were thus shown in the plasma, in addition to other expected heavy (e.g. O_2 and N_2) and light (electrons, photons) species. The acid properties are due to the occurrence in the gas phase of ON^\bullet , which gives rise to acidic species such as NO_2 , HNO_2 and HNO_3 at the liquid/gas interface. HNO_2 and HNO_3 occurrence was shown by water and sodium hydroxide solution treatments [11–13] and the brown gas NO_2 was also observed in the reactor. Similarly, oxidising effects in the liquid phase result from species such as HO^\bullet which was shown in our case [7,8] as in other kinds of humid air plasmas [15,16].

In this study, we focus on the chemical properties of humid air glidarc toward TBP to design a new process for spent solvent elimination [17].

2. Experimental section

2.1. Plasma treatment

As mentioned, the gliding arc device is largely described elsewhere [5–14,17,18]. A scheme of the experimental device is given on Fig. 1. The glidarc reactor consists in two aluminium diverging electrodes (E), symmetrically disposed with respect to a blowing gas nozzle (N). The feeding gas is provided by an air-compressor; the supplied airflow (545 l h^{-1}) bubbles through water filled Durand flask to saturate with water vapour.

When the electrodes are raised to a suitable voltage (10 kV), an arc forms between the electrodes. The airflow blows this arc, which glides along the electrodes until it is

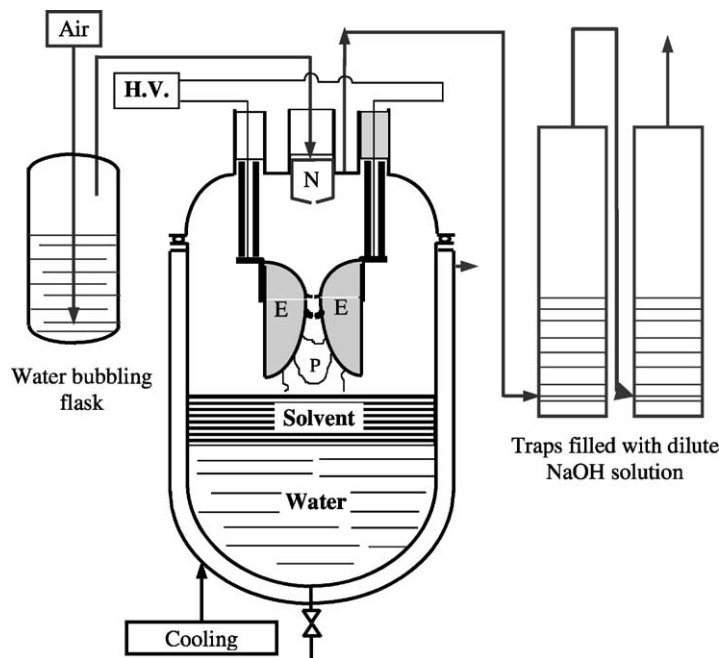


Fig. 1. Scheme of the experimental device.

short-circuited by a forming new arc. On breaking the arc turns from thermal to quenched plasma. A trail of non-thermal plasma is thus formed and is able to lick a liquid target.

In the present study, the liquid to be treated consists in an upper layer of TBP (50 ml) over water (750 ml). It is disposed in front of the plasma trail, in a 1 l reactor fitted with a cooling fluid circulation jacket. During the treatment, phosphoric acid yielded by oxidation of TBP drifts to the aqueous phase where it is extracted. After each hour of treatment, the reaction medium is stirred and allowed to decant. The aqueous phase is suitably diluted with a known factor, washed with octane to remove any trace of TBP. The phosphoric acid is then titrated by spectrophotometry according to a standard molybdenum procedure involving phosphomolybdate formation and reduction by ascorbic acid to a specific blue complex. The degradation yield may be then calculated from the phosphorus balance. In the same time, a 100 μ l sample of the organic phase is taken for dibutylphosphoric acid (HDBP) analysis by nuclear magnetic resonance spectroscopy (NMR). We followed the suitable ^{31}P NMR method developed by Uetake [19] with trimethylphosphate (TMP) as internal standard. Therefore, the sample is added to a standard solution of TMP in pyridine (1 ml). Spectra were recorded on a Bruker ARX spectrometer (400 MHz) with non-coupling mode.

2.2. Products analysis

At the end of the plasma treatment (i.e. when no more phosphoric acid is produced), the remaining organic products are extracted by ether (four times with 20 ml). The quantity of

remaining TBP is determined by gas chromatography (Varian 3400, fitted with a capillary column (stationary phase: 95% polydimethylsiloxane, 5% polydiphenylsiloxane) and flame ionisation detector) using diphenylmethane as internal standard. Further separation of the compounds formed during the plasma treatment involves classical operations.

- (i) Washing of the ether phase with aqueous 0.5 M NaOH (three times with 20 ml) to extract the organic acid products as their sodium salts.
- (ii) Acidifying of the obtained aqueous solution with 2.5 M H₂SO₄, saturating with NaCl, extracting into ether (four times with 20 ml) the molecular compounds present.
- (iii) Removing of the solvent in vacuum to perform IR analysis of the residue and gas chromatography analysis of the trimethylsilylester derivative (trimethylchlorosilane with hexamethyldisilazane and triethylamine method) [20]. Fourier transform infrared (FTIR) spectra (neat liquid) were recorded by using a NaCl cell.

A greyish white layer was found on the electrodes. This layer was removed carefully and a sample (0.18 g) was dissolved in a solution of 2 M NaOH (60 ml) and the mixture was allowed to stand overnight. The solution was neutralised with 2.5 M H₂SO₄ and diluted to 250 ml (solution B). Twenty milliliter of solution B were refluxed with 20 ml of 2.5 M H₂SO₄ to hydrolyse all pyrophosphate and polyphosphate which are possibly present. The solution was suitably diluted and phosphates were titrated according to the method previously used for phosphoric acid.

3. Results and discussion

3.1. Degradation kinetics

Fig. 2 reports the variations of the quantity of phosphoric acid formed for various treatment times. The relevant typical curve shows three parts. The first one (i.e. for $0 < t < 60$ min) contains only two points and is thus inconclusive. It may be an induction period related to the activation of TBP molecules by grafted oxygenated functions. Occurrence of an induction period was also observed in some other plasma treatments of both liquid [12,13] and solid targets [21]. The second part (Part II) is the most relevant: it is linear and fits with a zero-order process. A first approach of the process may be related to the assumption that the active species of the plasma react at the liquid surface on impinging at the target molecules. For neat organic liquid, the target molecules present at the surface are much more numerous than the impinging species, so that a major part of the gas species are involved in the reaction, and their number depends on the energy provided to the discharge. The resulting mechanism is zero-order in solute. Part III corresponds to the drastic decrease in the effective surface between the plasma and the TBP, when the volume of the organic phase becomes too low to cover the entire liquid surface and thus to maintain an efficient interface. This causes the decrease in the H₃PO₄ production rate, which tends to zero.

The zero-order degradation of TBP by plasma treatment in batch conditions may correspond to a surface oxidation process modelled (Fig. 3) on the basis of the assumptions.

- (i) The degradation process takes place at the plasma/TBP interface.

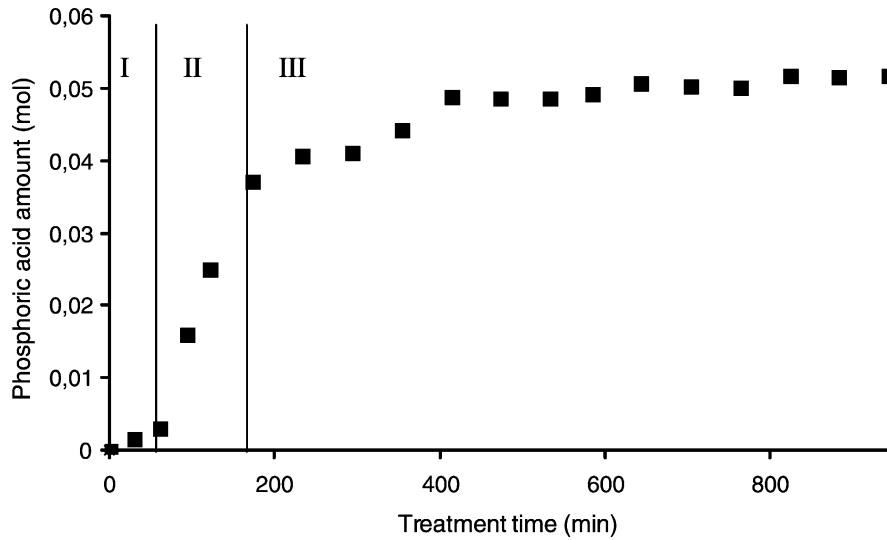


Fig. 2. Kinetics of degradation of TBP: plot of the yield in phosphoric acid vs. the treatment time.

- (ii) It involves a diffusion layer (thickness δ_L) at the plasma/TBP interface, which is defined by the gradient concentration of the active radicals formed at the plasma/liquid interface. For $x = \delta_L$ all the active species are consumed ($[\text{HO}^\bullet] = 0$).
- (iii) The degradation process is continuous, thus the thickness δ_L of the layer and the active species concentration in the plasma are constant.
- (iv) Phosphoric acid drifts to the aqueous phase.

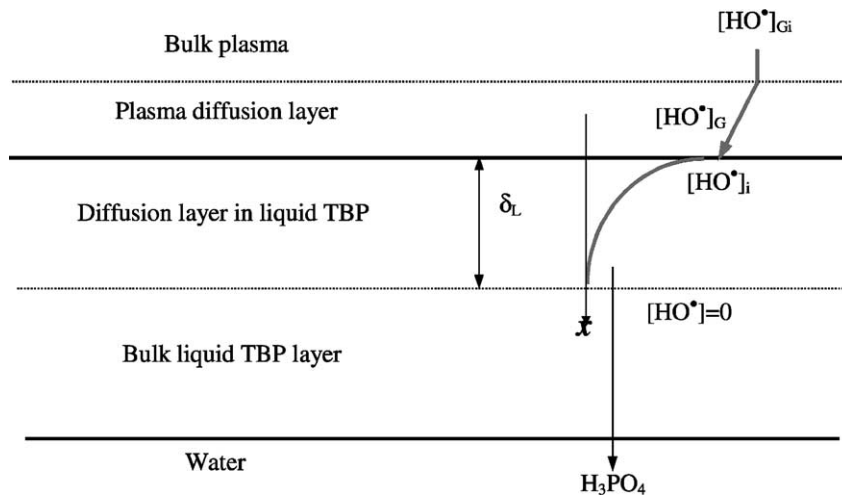
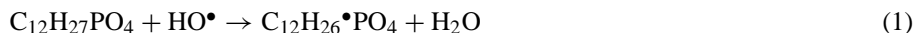
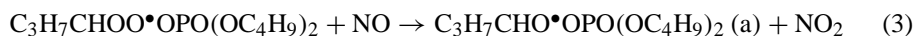


Fig. 3. Model of the diffusion reaction layer to account for the zero-order step.

Our chemical approach of the plasmachemical degradation of TBP involves the main active species formed in the discharge, i.e. HO•, and NO. Hydroxy radicals HO• which are the main highly oxidising species present in the gas phase (identified by emission spectroscopy, with NO species [7,8]) are able to remove one hydrogen atom from a TBP molecule, according to reaction (1),



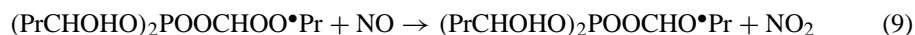
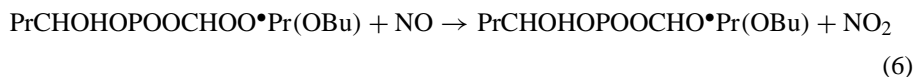
We assume that the reaction (1) is probably the rate-determining step, because the impinging radical concentrations are low compared with those of other species. In particular, the concentration of TBP is considered as constant in the reaction layer as it is in the bulk organic phase, since this phase is pure TBP. The suggested degradation process is following. The resulting radical $\text{C}_{12}\text{H}_{26}\bullet\text{PO}_4$ quickly reacts with oxygen and nitrogen oxide to give an alcoxy radical (a) according to mechanisms reported in the literature for further molecules [21–25].



The alcoxy radical undergoes hydrogen atom transposition to give a carbon radical with an hydroxybutyl chain (b).



This carbon radical undergoes two times the same process (reactions 5–9, Bu=C₄H₉, Pr=C₃H₇) followed by hydrogen transfer to an oxygen molecule to give bis- α -hydroxybutyl- α -oxobutylphosphate (c) (reaction 10).



This last compound reacts with water to give phosphoric acid (which is later extracted in the aqueous phase).



All the involved radicals are assumed to be found only in the δ_L -thick layer, so that $[\text{HO}\bullet] = 0$ for $x \geq \delta_L$. Therefore, the determining rate of reaction (1) is

$$V = k[\text{TBP}][\text{HO}\bullet] \quad (12)$$

or, with $k' = k[\text{TBP}]$,

$$V = k'[\text{HO}\bullet] \quad (13)$$

The mass transfer equation, which is presently

$$\text{div} \left[-D \frac{d[\text{HO}\bullet]}{dx} \vec{x} \right] = -k'[\text{HO}\bullet] \quad (14)$$

combined with Eqs. (12) and (13) leads to the radical concentration:

$$[\text{HO}\bullet] = \frac{[\text{HO}\bullet]_i}{1 - e^{-2\delta_L \sqrt{k'/D}}} (e^{-x\sqrt{k'/D}} - e^{(x-2\delta_L)\sqrt{k'/D}}) \quad (15)$$

for $0 \leq x \leq \delta_L$ and $[\text{HO}\bullet] = 0$ for $x > \delta_L$. D refers to the diffusion coefficient of $\text{HO}\bullet$ in TBP and $[\text{HO}\bullet]_i$, to the concentration of radicals at the interface. $[\text{HO}\bullet]_i$ is related to the concentration $[\text{HO}\bullet]_{\text{Gi}}$ in the plasma phase at the liquid surface by the Henry's law

$$K_H = \frac{[\text{HO}\bullet]_i}{[\text{HO}\bullet]_{\text{Gi}}} \quad (16)$$

Integrating the volumic rate of reaction (1) for $0 < x < \delta_L$ and using Eq. (15) leads to the degradation flow per surface unit:

$$\begin{aligned} v_s &= \int_0^{\delta_L} v \, dx = k' \int_0^{\delta_L} [\text{HO}\bullet] \, dx = \frac{\sqrt{k'D} K_H [\text{HO}\bullet]_{\text{Gi}}}{1 - e^{-2\delta_L \sqrt{k'/D}}} (1 - e^{-\delta_L \sqrt{k'/D}})^2 \\ &= k_g \text{ (mol m}^{-2} \text{ s}^{-1}) \end{aligned} \quad (17)$$

The mole number of phosphoric acid produced after a given treatment time (i.e. for $t \geq t_0$) is then:

$$n_{\text{H}_3\text{PO}_4} = S k_g (t - t_0) + n_0 \quad (18)$$

Eq. (18) involves the contact surface S between plasma and TBP and the induction time t_0 (Fig. 2, part I), during which n_0 moles of phosphoric acid form. S is constant during the linear part of the kinetic plot (Fig. 2, Part II). When the quantity of remaining TBP is not sufficient to ensure a permanent efficient contact surface S , the organic layer is broken and repelled to the reactor walls by the air flow. Thus, the surface S tends to zero and, therefore, so does the overall degradation rate (Fig. 2, Part III).

The model is a first attempt to explain the shape of the kinetic plot (and especially parts II and III). However, the lack of quantitative data and measurements reported in the literature prevents the development of a better model. The model presented here is based mainly on published radical degradation mechanisms [22–26]. However, it fails to explain the occurrence of the induction period t_0 , which was already observed for some other plasma treatments [12,21].

3.2. Analysis of outlet exhaust fumes and inorganic products characterization

We have monitored the occurrence of CO_2 in gaseous products during the plasma treatment with specific reagent tubes. Fig. 4 illustrates the relevant results (corrected by

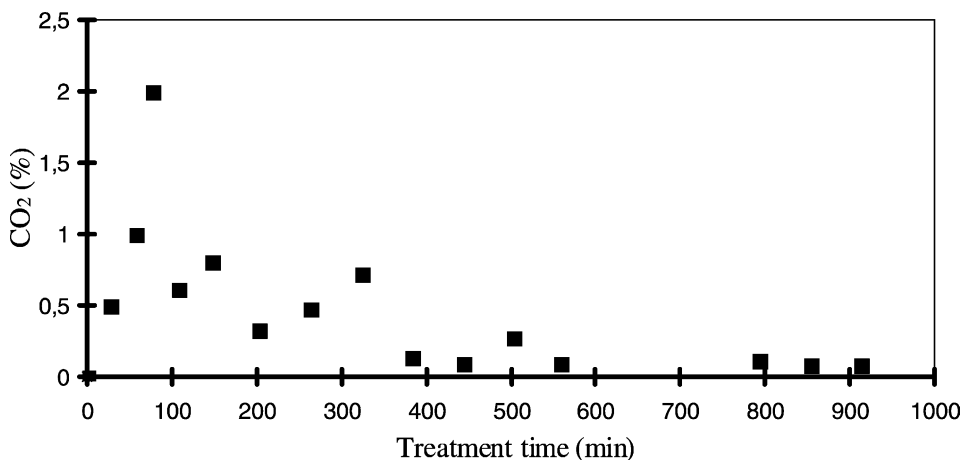


Fig. 4. Monitoring of CO₂ content in exhaust fumes.

subtraction of the inlet air content (0.05%)), and shows a CO₂ emission mostly during the second part of the kinetics; this gives an extra evidence of the degrading effect of the plasma.

However, the measured yield of H₃PO₄ (i.e. 28.2%) in the aqueous phase does not match the total phosphorus brought by initial TBP. We focused on the phosphorus balance and pointed out that white smokes were present in outlet exhaust fumes, especially during Part II of the kinetics. These fumes were trapped in aqueous NaOH solutions; phosphorus was found and titrated as phosphate, which gave substantial amount (11.4%). Organic matter was also subsequently extracted and the analysis showed non-degraded TBP (4.4%). these features agree with a loss of TBP by dynamic evaporation followed by oxidation of the vapours in the plasma phase to phosphoric oxide (i.e. P₄O₁₀) particles, which are swept along by the airflow without absorption by the aqueous phase in the reactor.

Additionally, another fraction (5.7%) of the TBP vapours underwent a local pyrolysis at the hot surface of the electrodes and gave metallic phosphate layer. Remaining TBP (15%) was also found in the reactor medium after the treatment.

Phosphorus and carbon distributions are gathered in Table 1 and show that 64.7% of the total phosphorus brought by the initial TBP is now recovered. at least 45% was converted

Table 1

Phosphorus and carbon distributions after treatment (percent of initial matter) after 900 min (15 h) treatment

	Phosphorus distribution (%)		Carbon distribution (%)
H ₃ PO ₄ in aqueous phase	28.2	CO ₂ (extrapolated)	52
Remaining TBP in the reactor	15	Remaining TBP in the reactor	15
Phosphate layer on the electrodes	5.7	TBP in exhaust fumes traps	4.4
Inorganic phosphate in exhaust fumes traps	11.4		
TBP in exhaust fumes traps	4.4		

into inorganic phosphates and 19.5% was not degraded. Smokes remain in the outlet of traps, which explains the deficit in the phosphorus balance.

These results confirm that the plasma treatment of TBP involves two surface processes.

- Degradation of liquid TBP caused by oxygenated radicals impinging at the liquid surface.
- Oxidation of TBP vapours near the surface, which gives phosphorus oxide particles.

3.3. Identification of a by-product

3.3.1. ^{31}P NMR monitoring

HDBP ($(\text{C}_4\text{H}_9\text{O})_2\text{POOH}$) is widely described as TBP degradation product [1,28,29]. Thus, we attempted to detect HDBP by means of ^{31}P NMR measurements. Fig. 5 actually reports typical spectra with a chemical shift 1.3–1.4 ppm higher than TBP, which is due to HDBP, and agrees with Uetake's result [19]. Integrating this signal leads to the HDBP quantity in the organic phase (Fig. 6).

For treatments shorter than 280 min, the concentration of HDBP is so low that it cannot be detected (Figs. 5 and 6). Its difficult to explain the “induction period” (for $t < 280$ min) followed by a very strong soaring to the maximum between 280 and 340 min, when 79% of the final phosphoric acid is formed and the zero-order kinetic step (Fig. 2) is finished. We think that when the contact surface between plasma and TBP decreases, the radical flow received by the TBP also decreases and becomes inadequate to degrade up to H_3PO_4 . Thus, partial degradation into HDBP then occurs. A fraction of HDBP may also be formed by acid hydrolysis of TBP [1,27], since phosphoric and nitric [12–14] acids may act as catalysts. Hydrolysis is therefore favoured at the end of the treatment, when the reaction medium becomes acidic enough. HDBP may also occur during the zero-order phase of the process (Fig. 2). However, HDBP is probably more sensitive to oxidation than TBP, due to the less hindered carbon chains than TBP, and may be degraded as soon as it forms. Therefore, its concentration remains too low to be detected. This agrees with the assumption of radical reaction with the TBP (reaction 1) as the slowest step. Temperature may also be involved in

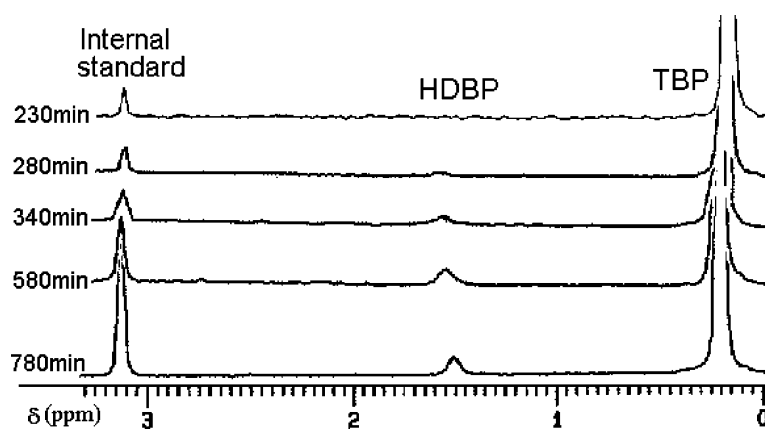


Fig. 5. ^{31}P NMR spectra of the organic phase sampled for several treatment times: the occurrence of HDBP is illustrated.

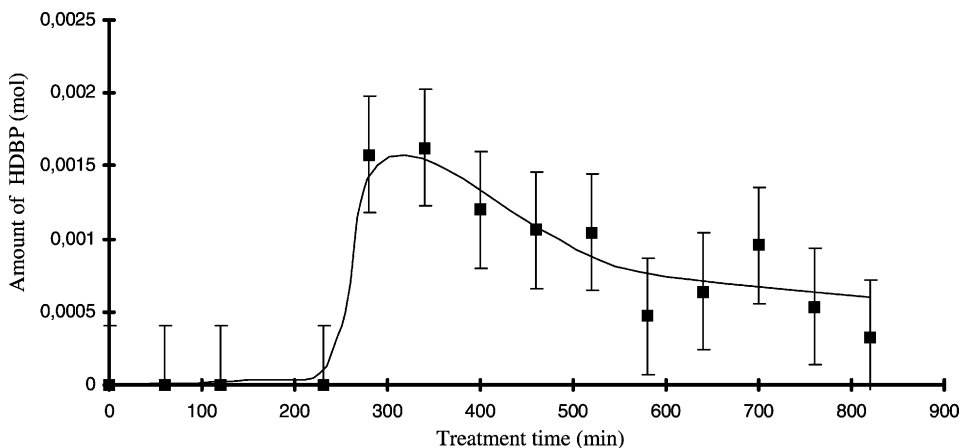


Fig. 6. Estimation of the HDBP amount in the organic phase from ^{31}P NMR spectra.

the process: a thermal gradient takes place between the electrodes and the reactor walls so that, when the organic phase is repelled to the reactor walls (i.e. at the end of the zero-order step), the temperature of the liquid decreases and degradation process may change and favour HDBP formation. After 350 min, globally, we have a slow decrease, but with strong fluctuations. When the TBP layer does not totally cover the aqueous surface, its distribution pattern may randomly fluctuate, which affects the kinetics.

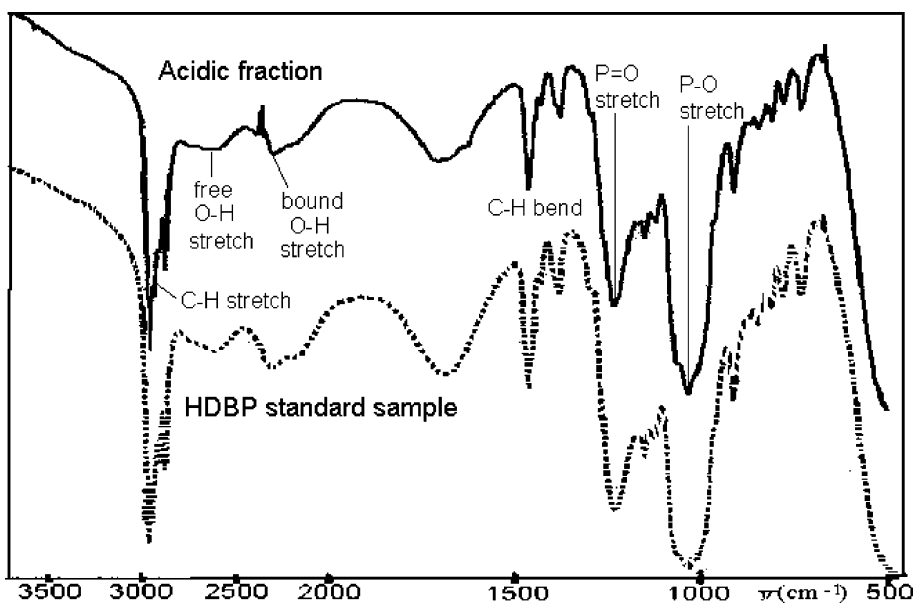


Fig. 7. Infrared spectra of the acidic organic fraction and of commercial HDBP.

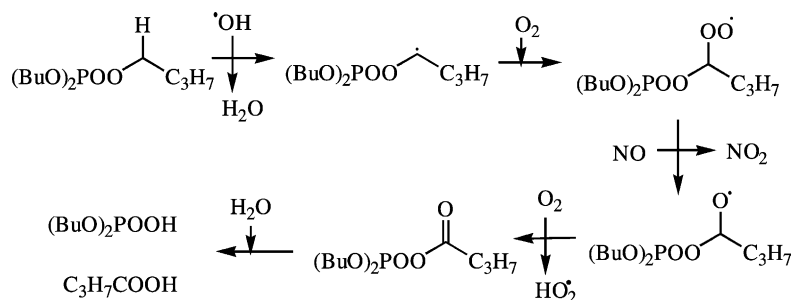


Fig. 8. Suggested mechanism for the formation of HDBP.

3.3.2. IR and GPC confirmation of the presence of by-product HDBP

The acid fraction of the organic phase was extracted and analysed by FTIR spectroscopy: Fig. 7 reports the spectrum, compared with HDBP standard and clearly shows that HDBP is the major component.

Additionally, the occurrence of this product was confirmed by gas phase chromatography by a trimethylsilylation procedure using a pure HDBP standard sample [1,20].

The reported results and a survey of the pertinent literature [22–26] lead us to suggest a mechanism for the formation of HDBP as the main by-product (Fig. 8), which takes into account the reactivity of the hydroxy radicals toward organic compounds.

4. Conclusion

A new plasma reactor of the gliding arc type (i.e. belonging to the non-thermal plasma family) was designed and used for the first time to degrade an organic waste solvent at atmospheric pressure and near ambient temperature. The treatment in humid air plasma was performed in batch conditions and concerns tributylphosphate, a rather stable extraction solvent, which is degraded mainly to CO_2 and H_3PO_4 . The degradation rate depends on both the flow of the highly oxidising species (e.g. HO^\bullet) formed in the plasma arc and the plasma/liquid contact surface. Since the flow of oxidising species is constant during the treatment (i.e. it depends only on the reactor and electrodes geometry, distance between electrodes and target, and humid air flow), the degradation obeys a zero-order kinetic law while the plasma/TBP contact surface is maintained constant. The rate is 10 mmol h^{-1} in forming H_3PO_4 in our working conditions. Dibutylphosphoric acid was identified as the main organic by-product, as in TBP degradation by other ways such as radiolysis [1,28,29]. Work is in progress to improve the degradation rate and to complete the phosphorus balance.

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