Chemical and photochemical degradation of acenaphthylene. Intermediate identification

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Abstract

Removal of acenaphthylene from water has been carried out by means of different treatments combining UV radiation, ozone and hydrogen peroxide. Ozonation alone or in conjunction with hydrogen peroxide (10^{-3} M) resulted in the highest elimination rates. Thus, conversions as high as 95–100% were obtained in less than 3 min with an ozone dose of 4.1×10^{-3} mol O_3 h^{-1} (flow rate 2×10^{-2} m^3 h^{-1}). Slightly lower efficiencies were experienced when using systems containing UV radiation.

By considering the kinetics of the direct photolysis of acenaphthylene and the UV/H_2O_2 system the photochemical reaction quantum yield ϕ_A ($4.0 \pm 0.1 \times 10^{-3}$ mol/photon) and the rate constant of the reaction of acenaphthylene with the hydroxyl radical $k_{OH,A}$ ($8.0 \pm 0.5 \times 10^9$ M^{-1} s^{-1}) were calculated.

Intermediates identified by GC/MS were in many cases similar regardless of the oxidation treatment used. Most of these by-products constituted oxygenated species of the parent compound (mainly ketones, aldehydes and carboxylic acids) that further degraded to low molecular, harmless end products. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polynuclear aromatic hydrocarbons (PAHs) constitute an important group of micropollutants, which can be found in different air, soil and water environments. Because

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some PAH compounds have been shown to cause carcinogen or/and mutagenic effects [1], several institutions, like the World Health Organisation, US EPA, etc., have established maximum concentrations for these organics in water [2]. In this sense, studies on removal technologies to reduce or degrade the presence of this type of contaminants in aquatic systems are valuable.

Oxidation treatments appear as a suitable way to eliminate PAHs from water. Thus, several works have been carried out on the use of classical oxidants like chlorine and chlorine dioxide [3,4], and more recent technologies based on the use of ozone, UV radiation and combinations with hydrogen peroxide [5–7].

The generation of the highly reactive hydroxyl radical (OH $\cdot$) in some of these treatments in conjunction with the direct action of ozone or/and the UV radiation have resulted in high PAHs degradation rates achieving conversions as high as 90% in just a few minutes. However, formation of oxygenated species that can be potentially hazardous is one of the drawbacks of these treatments, especially when utilising low residence times. Thereby, when assessing the efficiency of oxidising technologies to remove organic substances, it is also important from the environmental point of view to report the formation of intermediates and their presence in the final effluent.

Among the large number of compounds belonging to the family of PAHs, acenaphthylene presents one of the highest solubility of this group of substances [8] given the low number of rings and number of carbons. Since it is generally accepted that toxic effects (among other factors) are likely related to solubility of PAHs in water, in this work, degradation and intermediates formation from acenaphthylene oxidation have been studied using different technologies.

2. Experimental section

Experiments were carried out in a 1-l glass annular jacketed photochemical reactor already described elsewhere [9]. Oxygen or a mixture of ozone–oxygen was fed through a porous plate situated at the reactor bottom. Water pumped from a thermostatic bath circulated through the reactor jacket to ensure a constant temperature inside the reactor.

A low-pressure mercury vapour lamp was used for experiments carried out using UV radiation (254 nm.). Ozone was generated from pure oxygen by means of an SLO Constrema ozonator. In all cases, the reactor operated in semibatch mode. During experiments, samples were withdrawn regularly for analysis of the parent compound.

Acenaphthylene (85%) was purchased from Aldrich and was used as-received. Aqueous solutions of acenaphthylene were prepared in ultrapure water after saturation overnight with an excess of the organic and further filtration (45-μm Millipore filters) of the solution.

Analysis of acenaphthylene concentration was carried out by HPLC with a 1050 Hewlett Packard pump and a Rheodyne injector. The system was equipped with a 1046 Hewlett Packard programmable fluorescence detector (excitation and emission wavelengths of 226 and 333 nm, respectively). A Waters Nova-Pack C18 column was used utilising a mobile phase 50:50 (v/v) acetonitrile/water mixture with a flowrate of 1 ml min^{-1}. The retention time for acenaphthylene at these conditions was 15.2 min.

Intermediate identification was carried out with the following method: 1 l of the treated aqueous solution (90% conversion of the parent compound) was first acidified with hydrochloric acid (pH < 2) and extracted two times with 100 ml of methylene chloride. The organic phase was then dried with anhydrous sodium sulphate and concentrated in a rotary evaporator to less than 2 ml. In each analysis, 1 μl of sample was injected into a Hewlett Packard HP 5890 gas chromatograph coupled to a 5972 Mass Spectrometer operated in Scan mode. A 30 m-0.25 mm-0.25 μm film thickness HP-5MS cross linked 5% phenyl methyl silicone column was used. The oven temperature programme was set at 323 K for 2 min ramp up to 583 K (8 K min^{-1}) and 15 min at 583 K. The carrier gas was helium.

3. Results and discussion

3.1. Systems with UV radiation.

UV radiation has been used to degrade acenaphthylene either as a single system or in combination with ozone or hydrogen peroxide. Fig. 1 shows the evolution of the remaining normalized concentration of acenaphthylene with time for a series of experiments in duplicate conducted using UV radiation alone or in conjunction with ozone or hydrogen peroxide.

As can be observed from Fig. 1, application of UV radiation alone led to the poorest conversion results. Furthermore, although a number of authors [10,11] have proposed direct photodegradation of PAHs for water treatment, additional drawbacks can be encountered when applying this technology. The main limitation is that the target compound must efficiently absorb the light in competition with other organic and inorganic substances present in the media. In addition, degradation by-products may, in
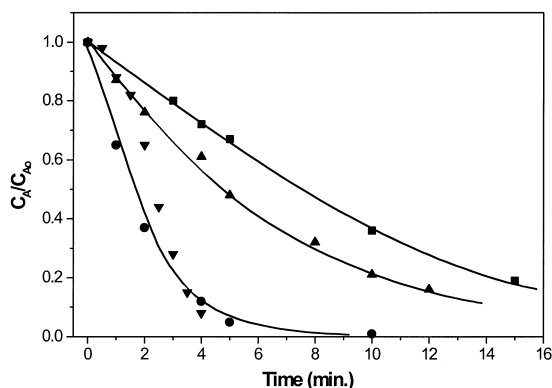

Fig. 1. Degradation of acenaphthylene in aqueous solution by different treatments. Evolution of the normalized remaining concentration with time. Conditions: $T = 293$ K, pH $= 7$, $C_{A0} = 1.73 \times 10^{-5}$ M. ■, UV ($I_0 = 3.48 \times 10^{-6}$ Einstein L^{-1} s^{-1}, $L = 4.5$ cm); ●, UV + H$_2$O$_2$ (10^{-3} M); ▲, UV + H$_2$O$_2$ (0.4 M); ▼, UV + O$_3$ ($P_{O3} = 500$ Pa, $k_L a = 3.5 \times 10^{-3}$ s^{-1}).

some cases, present a higher complexity and toxicity compared to the parent compound [12].

The combination of UV radiation with ozone (500 Pa partial pressure) or hydrogen peroxide (10^{-3} M) showed a comparable efficacy in acenaphthylene removal rate. Processes combining UV radiation and other oxidants like ozone or hydrogen peroxide show in most cases a higher efficacy to eliminate the parent compound and to form simpler oxygenated molecules of easier biodegradation. The reason for this is the generation of the non-selective hydroxyl radical, the principal oxidising agent in this type of treatments. Thus, after 5 min of treatment, only 33% conversion in acenaphthylene degradation was achieved in comparison to the 95% conversion obtained when using hydroxyl radical generating systems.

Kinetics of photolysis of acenaphthylene can be described by the following expression [9]:

$$-\frac{dC_A}{dt} = \phi_A \frac{\varepsilon_A C_A}{\sum_i \varepsilon_i C_i} I_0 \left[1 - \exp\left(-2.303 L \sum_i \varepsilon_i C_i \right) \right], \tag{1}$$

where: ϕ_A = photochemical reaction quantum yield (mol/photon); ε = extinction coefficient (M^{-1} cm^{-1}); I_0 = incident radiation flow (Einstein L^{-1} s^{-1}); C = concentration of UV radiation absorbing species (M); L = effective path of radiation in the photochemical reactor (cm); and subindexes A and i refer to acenaphthylene and any absorbing species present in the media, respectively.

If it is assumed that the main absorbing substance is the parent compound, then $\sum \varepsilon_i C_i \approx \varepsilon_A C_A$. The previous assumption is based on two points. First, although acenaphthylene used in this work was only 85% pure, the remaining 15% was acenaphthene whose extinction coefficient at 254 nm, $\varepsilon = 1333$ M^{-1} cm^{-1} [9], is much lower than the corresponding to acenaphthylene, $\varepsilon = 26\,941$ M^{-1} cm^{-1}, thereby at time zero it is found that acenaphthylene absorbs at least two order of magnitude more UV radiation than acenaphthene, $\varepsilon_{Acenaphthylene} 0.85 / \varepsilon_{Acenaphthene} 0.15 > 10^2$. Second, concentration of intermediates is significantly smaller than the acenaphthylene concentration if low conversions are considered.

Taking into account all the above reasons, Eq. (1) can be analytically integrated to give:

$$C_A - C_{A0} + \frac{1}{\alpha} \ln\left[\frac{1 - \exp(-\alpha C_{A0})}{1 - \exp(-\alpha C_A)} \right] = -I_0 \phi_A t, \tag{2}$$

where

$$\alpha = 2.303 L \varepsilon_A, \tag{3}$$

and C_{A0} is the acenaphthylene concentration at the start of the reaction.

Now from Eq. (2), it can be inferred that a plot of the left side vs time should yield a straight line of slope $-I_0 \phi_A$. This representation is shown in Fig. 2. Given the values of $I_0 = 3.78 \times 10^{-6}$ Einstein L^{-1} s^{-1} and $L = 4.5$ cm obtained by actinometry experiments [9]. The photochemical reaction quantum yield for acenaphthylene was calculated
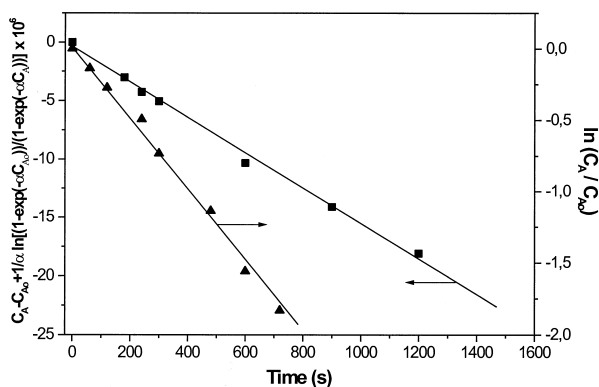
Fig. 2. Determination of kinetic parameters. ■, ϕ_A (Eq. 2); ▲, $k_{OH,A}$ (Eq. 17).

to be $\phi_A = (4.00 \pm 0.11) \times 10^{-3}$ mol/photon, which is of the same order of magnitude as other reported values for this type of compounds [9].

It has to be pointed out that the value of ϕ_A was obtained in photolysis experiments carried out in oxygen saturated water; however, a number of works published on PAH degradation, either with UV or sunlight radiation have claimed that the nitrogen purge of the aqueous solutions had no significant effects on degradation rates [9–11].

The higher reaction rate found when utilising the system UV/H_2O_2 is likely due to the combination of two possible degradation pathways, direct photolysis and reaction with hydroxyl radicals according to the following mechanism:

$$A + h\nu \rightarrow Products \tag{4}$$

$$H_2O_2 + h\nu \rightarrow 2OH \cdot \tag{5}$$

$$A + OH \cdot \rightarrow Products \tag{6}$$

$$H_2O_2 + OH \cdot \rightarrow \cdot HO_2 + H_2O \tag{7}$$

$$HO_2^- + OH \cdot \rightarrow \cdot HO_2 + OH^-. \tag{8}$$

Obviously Eqs. (4)–(8) represent a simplified scheme of the actual mechanism that involves other organic and inorganic radical species, organic peroxides, excited states of different molecules, etc., depending on the parent compound nature [13,14].

If the mechanism given by Eqs. (4)–(8) is assumed, the kinetics of acenaphthylene degradation can be expressed as:

$$-\frac{dC_A}{dt} = \phi_A \frac{\varepsilon_A C_A}{\sum_i \varepsilon_i C_i} I_0 \left[1 - \exp\left(-2.303 L \sum_i \varepsilon_i C_i \right) \right] + k_{OH,A} C_{OH} C_A, \tag{9}$$

where C_{OH} is the hydroxyl radical concentration and $k_{OH,A}$ the rate constant of the reaction between this species and acenaphthylene. From the mechanism of Eqs. (4)–(8),

it is deduced that the only route of hydroxyl radical generation is through photolysis of hydrogen peroxide:

$$-\frac{dC_H}{dt} = \phi_H \frac{\varepsilon_H C_H}{\sum_i \varepsilon_i C_i} I_0 \left[1 - \exp\left(-2.303 L \sum_i \varepsilon_i C_i\right)\right], \tag{10}$$

where the subindex H stands for hydrogen peroxide. Since each molecule of H_2O_2 produces two hydroxyl radicals, by applying the steady-state hypothesis to hydroxyl radical concentration, it is obtained:

$$C_{OH} = 2\phi_H \frac{\varepsilon_H C_H}{\sum_i \varepsilon_i C_i} I_0 \frac{\left[1 - \exp\left(-2.303 L \sum_i \varepsilon_i C_i\right)\right]}{\sum_i k_{OH,j} C_j}, \tag{11}$$

$k_{OH,j}$ being the rate of the reaction of any species j with the hydroxyl radical. Moreover, if a high concentration of hydrogen peroxide is used (i.e. 0.4 M, up triangles in Fig. 1) it can be assumed, without incurring in significant error, the following expressions:

$$\Sigma \varepsilon_i C_i \approx \varepsilon_H C_H \gg \varepsilon_A C_A \tag{12}$$

$$\Sigma k_{OH,i} C_i \approx k_H C_H. \tag{13}$$

Under these conditions, it is evident that UV radiation is totally absorbed by hydrogen peroxide and, subsequently, acenaphthylene removal kinetics becomes:

$$-\frac{dC_A}{dt} = k_{OH,A} \frac{2\phi_H I_0}{k_{OH,H} C_H} C_A. \tag{14}$$

Eq. (14) was derived by applying the simplification:

$$1 - \exp\left(-2.303 L \sum_i \varepsilon_i C_i\right) \approx 1. \tag{15}$$

It has to be noted that in Eq. (14), the value of $k_{OH,H}$ accounts for Eqs. (7) and (8), since the rate constant for these reactions differ in two orders of magnitude (see Eq. 16):

$$k_{OH,H} = \frac{2.7 \times 10^7 + 7.5 \times 10^9 10^{pH-pK}}{1 + 10^{pH-pK}}, \tag{16}$$

where $pK = 11.8$. Eq. (14) can be integrated to yield:

$$-\ln\frac{C_A}{C_{A0}} = k_{OH,A} \frac{2\phi_H I_0}{k_{OH,H} C_H} t. \tag{17}$$

Thus, a plot of the left term of Eq. (17) vs time should give a straight line (see Fig. 2). From the slope of this line a value of $(8.0 \pm 0.5) \times 10^9$ M^{-1} s^{-1} was calculated for $k_{OH,A}$. This value was similar to the one previously reported for acenaphthene of $(8.8 \pm 0.3) \times 10^9$ M^{-1} s^{-1} [15].

The system O_3/UV gave similar conversions to that obtained when utilising UV/H_2O_2. In this case, degradation of acenaphthylene is due to three different routes, direct reaction with ozone, photodegradation and radical reaction through the following mechanism:

$$H_2O + O_3 + h\nu \rightarrow H_2O_2 + O_2 \tag{18}$$

$$HO_2^- + O_3 \rightarrow \cdot HO_2 + \cdot O_3^- \tag{19}$$

$$OH^- + O_3 \rightarrow \cdot HO_2 + \cdot O_2^-. \tag{20}$$

Eqs. (18)–(20) and the direct photolysis of hydrogen peroxide (Eq. 5) initiate a radical mechanism generating the hydroxyl radical, which reacts with acenaphthylene through reaction (6). No dissolved ozone was detected indicating a rapid reaction of this species either with acenaphtylene (see Section 3.2) or by absorbing UV radiation.

3.2. Systems without UV radiation

Ozonation of acenaphthylene was carried out in the presence and absence of a free radical inhibitor (*tert*-butyl alcohol) to ascertain the routes of degradation of this compound. Free radicals in ozonation processes are produced in reaction (20) and by the presence of other possible initiators contained in the solution.

From Fig. 3, it can be observed that the addition of 10^{-2} M of *tert*-butyl alcohol did not lead to significant differences in acenaphthylene degradation rates, indicating that this compound is eliminated mainly through direct reaction with ozone. Again, no dissolved ozone was detected until the PAH was completely removed from the solution.

Addition of hydrogen peroxide in the ozonation process is aimed at the generation of radicals by reaction of the anionic form of hydrogen peroxide with the ozone molecule (Eq. 19). In this work, a slight worsening of the acenaphthylene elimination rate was
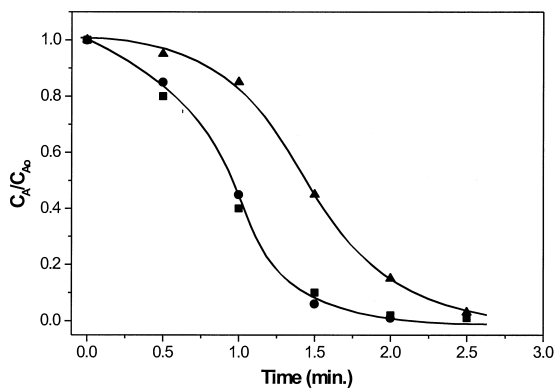
Fig. 3. Degradation of acenaphthylene in aqueous solution by different treatments. Evolution of the normalized remaining concentration with time. Conditions: $T = 293$ K, pH = 7, $C_{Ao} = 1.73 \times 10^{-5}$ M, $k_L a = 3.5 \times 10^{-3}$ s^{-1}, $P_{O3} = 500$ Pa. ▲, $O_3 + H_2O_2$ (10^{-3} M); ●, O_3; ■, $O_3 + tert$-butyl alcohol (10^{-2} M).

experienced when hydrogen peroxide was added to the medium; however, similar conversion to the one obtained with ozone alone was observed after 2.5-min treatment.

A comparison of the different systems used in this work from data obtained after 2 min of oxidation was completed. Thus, conversion values of roughly 16%, 50%, 50%, 85% and 99% were obtained for the UV, UV/H_2O_2, UV/O_3, O_3/H_2O_2 and O_3 treatments, respectively. Therefore, it can be concluded that among systems using ozone, single ozonation is the most effective method to remove acenaphthylene from water environments. Broadly speaking, the presence of UV radiation in the method used led to poorer results if compared to treatments with ozone and ozone/hydrogen peroxide. However, to find out the most efficient and economical treatment, a deeper study of the different technologies should be carried out using a wider range of conditions. Not only a comparison of energy and chemical costs vs acenaphthylene removal must be conducted, but also the final toxicity of the effluent has to be accounted for. Also, the presence of promoting or scavenging substances, solids in suspension, etc., in real waters must be considered when using a determined process.

3.3. Identification of intermediates

Table 1 shows the main intermediates identified by GC/MS. It is noticed that a similarity in the nature of intermediates formed regardless of the method of acenaphthylene degradation used. The presence of oxygenated molecules in the photodegradation of acenaphthylene can be attributed to thermal photooxygenation, either involving the

Table 1
Intermediates identified in the degradation of acenaphthylene by different treatments
X = Detected.

Compound	UV	O_3	UV/H_2O_2	H_2O_2/O_3	UV/O_3
2-methyl naphthalene	X	X	X		X
1-methyl naphthalene	X		X		
2-ethen-naphthalene	X	X	X	X	X
1,7-dimethyl naphthalene	X	X	X		X
2,7-dimethyl naphthalene	X	X	X		X
1-naphtalen carboxy aldehyde	X	X	X	X	X
dibenzofurane	X	X	X	X	X
1H,2H-1-oxaacenaphthylee-2-one	X	X	X	X	X
2-ethoxy-3-methoxyphenol	X		X	X	
1,1′-biphenyl 4-carboxyaldehyde	X		X	X	X
1,1′-biphenyl 2,2′diol	X				
1,2-acenaphthylenedione	X	X	X		
1H,3H-naphthen (1,8 cd) pyran 1-one	X	X	X	X	X
naphthalenecarboxylic acid	X	X	X	X	X
1,8-naphthalic anhydride	X	X	X	X	X
o-hydroxybiphenyl		X	X		X
1(3H)-isobenzofuranone				X	X
2-hydroxy-1-naphtalen carboxyaldehyde					X
benzaldehyde					X
2-methyl-benzaldehyde					X

direct reaction of an excited state of the organic molecule with oxygen, to form peroxides (Eq. 21), or by transference of the excitation energy to molecular oxygen, to generate an excited state of this species [12], usually in a singlet state (Eqs. 22 and 23).

$$A^* + O_2 \rightarrow AO_2 \rightarrow \text{Products} \tag{21}$$

$$A^* + O_2 \rightarrow A + O_2^* \tag{22}$$

$$A + O_2^* \rightarrow AO_2 \rightarrow \text{Products.} \tag{23}$$

Organic peroxides formed in the above mechanism may decompose and initiate a radical chain mechanism. However, other authors have reported the negligible role of oxygen in the photodegradation of PAHs [9,11]. Thus, photolysis of these compounds would be related to the formation of radical cation intermediates or involvement of the solvent (water) in the mechanism.

The formation of some compounds like furanes, biphenyls, pyranes, etc., suggests an increase in toxicity of the effluent if compared to the parent compound. Nevertheless, application of longer times of reaction (up to 30 min) resulted in the total disappearance of intermediates to form harmless final products such as low molecular organic acids (acetic, oxalic, etc.).

4. Conclusions

Acenaphthylene has been successfully removed by different water treatments involving the use of ozone, UV radiation and hydrogen peroxide. Among them, ozonation has been shown to degrade this compound in just 2 min, utilising an ozone partial pressure of 500 Pa at a flowrate of 2.0×10^{-2} m^3 h^{-1}. In the presence of ozone, the hydroxyl radical action seems to be negligible since the addition of initiators (hydrogen peroxide) or inhibitors (*tert*-butyl alcohol) had no significant effects on the degradation rate of acenaphthylene.

Although with a lower efficacy than the ozonation–hydrogen peroxide process, the systems UV/H$_2$O$_2$ and UV/O$_3$ also removed acenaphthylene from water at an acceptable reaction rate. By considering the kinetics of the UV/H$_2$O$_2$ treatment with a high concentration of hydrogen peroxide, the rate constant of the reaction between acenaphthylene and the hydroxyl radical was found to be $(8.0 \pm 0.5) \times 10^9$ M^{-1} s^{-1}.

Also, from the direct photolysis of this PAH the photochemical reaction quantum yield was obtained $(4.00 \pm 0.11 \times 10^{-3}$ mol/photon).

Intermediates found by GC/MS are, in general, oxygenated species of the parent compound, keeping the naphthalenic structure in some cases and generating heterocycles like furanes and pyranes in other cases. However, if the residence time of the aqueous solution in the reactor is enlarged, intermediates are also degraded leading to harmless, low molecular end products.

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