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Photocatalytic oxidation of polycyclic aromatic hydrocarbons: Intermediates identification and toxicity testing

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic pollutants and their low water solubility limits their degradation in aqueous solution. The presence of water-miscible solvent such as acetone can increase the water solubility of PAHs, however acetone will also affect the degradation of PAH. In this study the effects of acetone on the photocatalytic degradation efficiency and pathways of 5 selected PAHs, namely naphthalene (2 rings), acenaphthylene (3 rings), phenanthrene (3 rings), anthracene (3 rings) and benzo[a]anthracene (4 rings) were investigated. The Microtox® toxicity test was used to determine whether the PCO system can completely detoxify the parental PAHs and its intermediates. The addition of 16% acetone can greatly alter the degradation pathway of naphthalene and anthracene. Based on intermediates identified from degradation of the 5 PAHs, the location of parental PAHs attacked by reactive free radicals can be correlated with the localization energies of different positions of the compound. For toxicity analysis, irradiation by UV light was found to induce acute toxicity by generating intermediates/degradation products from PAHs and possibly acetone. Lastly, all PAHs ($10\,mg\,l^{-1}$) can be completely detoxified by titanium dioxide ($100\,mg\,l^{-1}$) within 24 h under UVA irradiation ($3.9\,mW\,cm^{-2}$).

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are fused-ring compounds consisting of carbon and hydrogen atoms, arranged in either a linear, angular or cluster structure. PAHs are mostly generated from anthropogenic sources; including combustion of coal and oil [1], waste incineration and motor vehicle emissions [2]. Due to their high toxicity, carcinogenic and mutagenic effects and environmental persistency [2], 16 PAHs have been listed by the United States Environmental Protection Agency and by the European Community as priority environmental pollutants [3]. Photocatalytic oxidation (PCO), one of the many advanced oxidation processes, relies on the generation of •OH by photocatalysts (e.g. titanium dioxide, TiO_2) to trigger oxidative degradation.

Acetone, a water-miscible organic solvent, helps PAHs contact a photocatalyst more readily to trigger PCO degradation in aqueous solution. However, a reaction between acetone and •OH generated occurred. According to Caralp et al. [4], they reported that there were two main reactions concerning acetone and •OH:

$$^{\bullet}OH + CH_3C(O)CH_3 \rightarrow {}^{\bullet}CH_3C(O)CH_2 + H_2O \quad (1)$$

$$^{\bullet}OH + CH_3C(O)CH_3 \rightarrow CH_3COOH + {}^{\bullet}CH_3 \quad (2)$$

Some studies have experimentally shown that the major pathway for the reaction between acetone and •OH is shown in Eq. (1), i.e. production of acetonyl radicals [5,6]. Thus, these acetonyl radicals may compete with the reactants (i.e. PAHs) for •OH leading to a decrease in degradation efficiency of PAHs, or they may react with PAHs and carry out a different degradation pathway. Therefore, the effect of acetone on PAHs degradation was studied.

As mentioned before, PCO is a process that mainly relies on the generation of reactive •OH to trigger oxidative degradation. Other reactive species such as superoxide radical anions ($^{\bullet}O_2^-$) and h^+ on TiO_2 molecules also leads to the formation of detected intermediates formed by irradiation. The electron distribution over PAH molecules is then significant for the reactive positions of the molecule that can be attacked in the PCO reaction [7]. Dewar's reactivity number, N_u, one of the several reactivity indices, reflects the localization energy and hence reactivity of a particular position on PAHs [8].

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In this study, the degradation pathways of 5 PAHs, namely naphthalene (2 rings), acenaphthylene (3 rings), phenanthrene (3 rings), anthracene (3 rings) and benzo[a]anthracene (4 rings), by PCO degradation (in 1% acetone) were investigated. In addition, 16% acetone (regarded as high acetone level) was added to the PCO systems to study the effect of acetone on the degradation pathways of PAHs. The correlation between the localization energy and reactivity of different positions of PAHs was studied. Lastly, the Microtox® test was also carried out to determine the detoxifying ability of the PCO system for these PAHs and their intermediates.

2. Materials and methods

2.1. Chemicals

Naphthalene, acenaphthylene, phenanthrene, anthracene and benzo[a]anthracene were purchased from different companies. Naphthalene and anthracene were bought from BDH (Poole, England) and Merck (Darmstadt, Germany), respectively. Acenaphthylene was purchased from Aldrich (St. Louis, USA), while phenanthrene and benzo[a]anthracene were from Sigma (St. Louis, USA). Titanium dioxide (TiO_2) was obtained from Degussa (Frankfurt, Germany), which is a non-porous mixture of 70% anatase and 30% rutile, with a BET surface area of 50 $m^2\,g^{-1}$ and an average particle size of 30 nm. Dichloromethane from Mallinckrodt (Phillipsburg, USA) and acetone from Labscan (Bangkok, Thailand) were HPLC grade. PAHs were dissolved in acetone to make a stock solution. A 100 ml reaction mixture of 10 $mg\,l^{-1}$ PAHs and 100 $mg\,l^{-1}$ TiO_2 were prepared for PCO reaction, and additional acetone was added in order to achieve required acetone level.

The following compounds were used for estimating the percentage yield of some intermediates generated during PCO reactions: 1,4-naphthalenedione, 9,10-phenanthrenedione, 9,10-anthracenedione, benzo[a]anthracene-7,12-dione and 1,2-benzenedicarboxaldehyde (Appendix A). The first four compounds were purchased from Aldrich (St. Louis, USA), while the last one was from Sigma (St. Louis, USA).

2.2. Photocatalytic reactor

PCO was conducted in a customized photocatalytic reactor, which consists of a stainless steel cylinder and control panel. Inside the cylinder, four 15-W UV lamps, purchased from Cole-Parmer International (Vernon Hills, USA) with emission peak at 365 nm, were placed around a Pyrex column. During the PCO process, ambient air was pumped at 200 $cm^3\,min^{-1}$ into the reaction mixture for the purpose of aeration and mixing. Cooling fans at the bottom of the reactor was used to prevent the reactor from overheating. The UV lamps used in the experiment emitted various intensities of UV light of different wavelengths: UVA = 3.9 $mW\,cm^{-2}$; UVB = 1.1 $mW\,cm^{-2}$ and UVC = 0.3 $mW\,cm^{-2}$.

2.3. Identification and quantification of PAHs and their intermediates

At various time intervals, a 10 ml sample was collected from the reactor and transferred into a glass extraction tube for extraction using 10 ml dichloromethane. After discarding the aqueous phase, the organic phase was concentrated by N-evaporator to near dryness (Associates Incorporation, Berlin, USA). The residue was then redissolved in 40 μl dichloromethane and filtered through a 0.45 μm PTFE membrane (Whatman International Limited, Maidstone, England). No additional stabilization procedure was done after extraction but the samples were analysis as soon as possible, the whole extraction process takes about 1 h. The extract was then stored at −20 °C until analysis.

PAHs and their intermediates were analyzed by a gas chromatograph (GC) (HP6890) equipped with a capillary column (HP-5 column, 30 m × 0.32 mm × 0.25 μm) and a mass selective detector (MS) (5973N) with the HP Chemstation software (Hewlett Packard Corporation, CA, USA). Spiltless (2.0 μl) injection was carried out by an auto-injector (HP7683, Hewlett Packard Corporation, CA, USA) with a temperature of 250 °C. After an isothermal period of 1 min at 50 °C, the oven temperature was increased to 300 °C at a rate of 5 °C min^{-1} and held for 5 min. The solvent delay was set at 3 min. The scan range was from m/z 40 to m/z 400 at 2.08 scan s^{-1}. The NIST98 MS library was used for species identification as a supplement for mass spectral and retention time characteristics. All library-matched species exhibited a degree of match better than 90%.

2.4. Toxicity analysis

A 5 ml sample was first filtered through glass microfibre filters (GF-C, Whatman International Ltd., Maidstone, England). The pH of the sample was adjusted to approximately 6–8. The test was performed by a Microtox® toxicity analyzer (M500, Azur Environmental, Carlsbad, USA) following the protocols for the basic or 100% test, according to the standard operating procedure [9]. The Microtox® reagents, reconstitution solutions, osmotic adjusting solution (OAS), diluent and cuvettes used were all purchased from Azur Environmental (Carlsbad, USA).

3. Results and discussion

3.1. Identification of intermediates

For each PAH used in this study, the abundance of intermediates measured by GC–MS was recorded to obtain a general trend of intermediates produced with irradiation time (Fig. 1). The intermediates detected and degradation pathways suggested were not complete since some intermediates were short-life and cannot be detected in GC–MS analysis. The relevant information of selected PAHs and their intermediates produced during the PCO reaction is shown in Table 1. The percentage yield of some intermediates for selected PAHs is measured in Appendix A as a reference. The maximum yield of intermediates can be up to 40%, in the case of PCO degradation of anthracene. The common intermediates found during PCO reaction were alcohol, ketone, quinone, aldehydes and benzopyrone. PCO reaction was usually started by hydroxylation of PAHs to form an alcohol. After a series of oxidation, smaller molecules of intermediates were resulted. The degradation pathways of 5 PAHs were proposed and shown in Fig. 2.

3.1.1. Effect of acetone level

The effect of acetone level on the photocatalytic degradation of PAHs was conducted in the presence of 1 and 16% of acetone. Acetone was added because PAHs were highly hydrophobic and with very low water solubility, adding acetone can improve the solubility of PAHs in the reaction mixture. The chose of these acetone concentrations was based on our preliminary results (data not shown) and the results of a previous study [10]. The results showed that the addition of 16% acetone can cause an accumulation of intermediates and this may allow us to find out more possible intermediates and hence propose a more complete degradation pathway. For example, higher concentrations and more types of intermediates were found in degradation of naphthalene with the high acetone level (Fig. 1(a) and Table 1(a)). Moreover, the times required for degradation of parental compounds were either not changed significantly or decrease. Similar findings were reported in the previous study on the photolysis of another azo dye, Disperse Red 13 [10]. In that study, the authors found that increasing the concentration of ace-

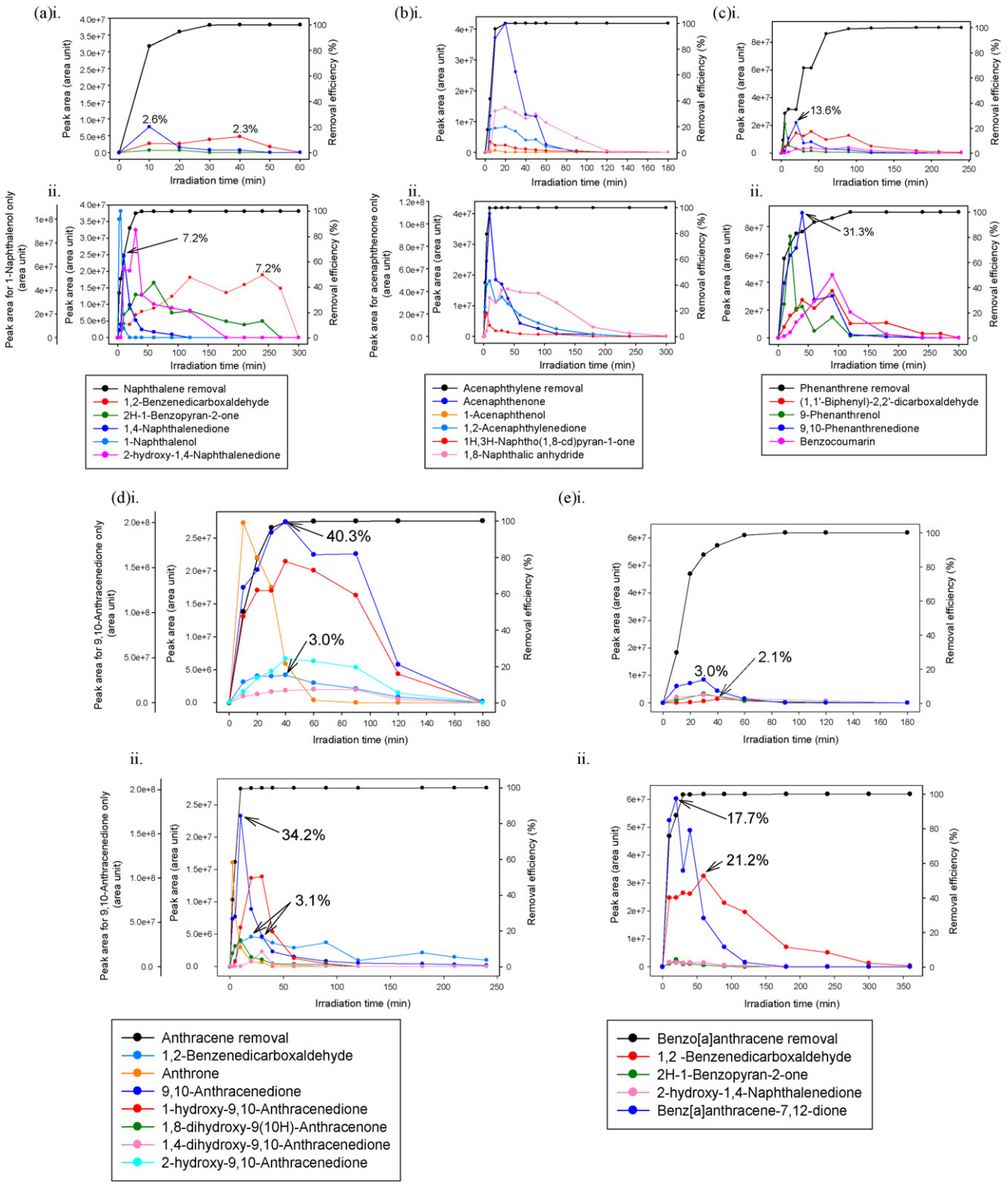

Fig. 1. Peak area of intermediates produced during PCO of selected PAHs: (a) naphthalene, (b) acenaphthylene, (c) phenanthrene; (i) represents intermediates identified under reaction condition with 1% acetone, (ii) represents intermediates identified under reaction condition with 16% acetone. The maximum percentage yields of some intermediates produced during PCO reaction were shown. Peak area of intermediates produced during PCO of selected PAHs: (d) anthracene and (e) benzo[a]anthracene; (i) represents intermediates identified under reaction condition with 1% acetone, (ii) represents intermediates identified under reaction condition with 16% acetone. The maximum percentage yields of some intermediates produced during PCO reaction were shown.

tone from 0 to 2 M will increase the reaction rate constant, and further increase the acetone concentration will cause inhibition of reaction. In our experiment, increasing the acetone concentration from 1% (~0.136 M) to 16% (~2.176 M) caused an increase of degradation of the parental compounds. The study also suggested that acetone will provide an alternative pathway for the photolysis of dye, but the reaction product was the same as without acetone. In our study on PAH degradation, the intermediates detected were also similar in the two concentrations tested, only the amount detected showed a difference.

3.2. Reactive sites of PAHs

Dewar's reactivity number, N_u, one of the several reactivity indices, reflects the localization energy and hence reactivity of a particular position on PAHs [8]. The smaller the N_u value, the lower the activation energy required, hence the higher the reactivity which results. Fig. 3 shows the (a) numbering and (b) N_u (Dewar) values of PAHs.

For naphthalene, the N_u value of position 1 is smaller than that of position 2, which means position 1 is more easily attacked by reactive oxygen species. In this study, only 1-naphthalenol was found. However, in a similar study conducted by Lair et al. [11], both types of naphthols were detected, but mainly 1-naphthalenol. Therefore, it was demonstrated that reactivity is correlated to the localization energy at a point on the molecule.

All intermediates found were derived from reactions of •OH attacking at the position 9 and/or 10 of phenanthrene. The N_u values of the positions 9 and 10 are slightly lower than that of the others. This indicates that most reactions take place at these two positions. A simple reason would be the better arrangement of electrons over the aromatic rings resulted upon attack. This modified form can become more stable by providing two peripheral delocalized sextets of electrons [12].

The N_u values for the positions of PAH molecules can help us to explain the degradation pathway of anthracene. The positions 9 and 10 are preferentially attacked, with 9,10-anthracenedione as the most abundant intermediate, as extra stability was gained for the intermediate formed upon attack at these positions by interaction with adjacent delocalization systems [12]. Ozonation, a chemical oxidation, shares some similarity with PCO reactions in that ozone reacts with PAHs by either substitution or ring opening. Yao et al. [13] agreed that the location of ozone attack is correlated with the lowest atom- or bond-localization energies of the target compound. Thus, 9,10-anthracenedione was also a common ozonation intermediate [14,15]. For the same reason, it was identified as an intermediate of photolysis of anthracene with oxygen supply [16,17]. Hydroxylation on the position 1 was also preferred because of a smaller N_u. The higher concentration of 1-hydroxy-9,10-anthracenedione detected is evidence of this.

As mentioned before, similar intermediates can be found in ozonation and PCO reactions of benzo[a]anthracene. In the study of Yao et al. [13], two types of ozonation intermediates of benzo[a]anthracene were detected: (1) phenyl–naphthyl type (bond attack at the positions 5 and 6) and (2) quinone type (atom attack at the positions 7 and 12). Yao et al. [13] agreed that the location of the ozone attack was related to the lowest atomic- and bond-localization energies of the compound. The N_u values of the positions 7 and 12 were the lowest of all. Benzo[a]anthracene-7,12-dione, belonged to type (2) intermediates of ozonation, was observed here. Yao et al. [13] also found that the bond-attack type of reaction occurred at the bond between the positions 5 and 6 because of its low energy and, therefore, resulted in ring cleavage. Likewise, these two positions have the second lowest N_u value. Nevertheless, type (1) intermediates were not found in our study.

All intermediates of acenaphthylene were generated from the reaction at the unsaturated bond of the cyclopentafused ring of ace-

Table 1
Information about selected PAHs and their intermediates produced during PCO degradation identified by GC–MS.

No.	Retention time (min)	Empirical formula	Name	Remarks
(a)				
1	13.3	$C_{10}H_8$	Naphthalene (parental compound)	x, y
2	14.9	$C_8H_6O_2$	1,2-Benzenedicarboxaldehyde	x, y
3	19.1	$C_9H_6O_2$	2H-1-benzopyran-2-one	x, y
4	19.3	$C_{10}H_6O_2$	1,4-Naphthalenedione	x, y
5	22.0	$C_{10}H_8O$	1-Naphthalenol	y
6	22.6	$C_{10}H_6O_3$	2-Hydroxy-1,4-naphthalenedione	y
(b)				
7	20.4	$C_{12}H_8$	Acenaphthylene (parental compound)	x, y
8	25.4	$C_{12}H_8O$	Acenaphthenone	x, y
9	25.5	$C_{12}H_{10}O$	1-Acenaphthenol	x
10	29.9	$C_{12}H_6O_2$	1,2-Acenaphthylenedione	x, y
11	30.2	$C_{12}H_8O_2$	1H,3H-naphtho(1,8-cd)pyran-1-one	x, y
12	33.0	$C_{12}H_6O_3$	1,8-Naphthalic anhydride	x, y
(c)				
13	28.2	$C_{14}H_{10}$	Phenanthrene (parental compound)	x, y
14	29.9	$C_{14}H_{10}O_2$	(1,1′-Biphenyl)-2,2′-dicarboxaldehyde	x, y
15	31.4	$C_{13}H_8O_2$	Benzocoumarin	x, y
16	34.8	$C_{14}H_{10}O$	9-Phenanthrenol	x, y
17	35.7	$C_{14}H_8O_2$	9,10-Phenanthrenedione	x, y
(d)				
18	14.9	$C_8H_6O_2$	1,2-Benzenedicarboxaldehyde	x, y
19	28.1	$C_{14}H_{10}$	Anthracene (parental compound)	x, y
20	31.4	$C_{14}H_{10}O$	Anthrone	x, y
21	31.9	$C_{14}H_8O_2$	9,10-Anthracenedione	x, y
22	33.8	$C_{14}H_8O_3$	1-Hydroxy-9,10-anthracenedione	x, y
23	34.6	$C_{14}H_{10}O_3$	1,8-Dihydroxy-9(10H)-anthracenone	y
24	35.9	$C_{14}H_8O_4$	1,4-Dihydroxy-9,10-anthracenedione	x, y
25	39.2	$C_{14}H_8O_3$	2-Hydroxy-9,10-anthracenedione	x
(e)				
26	14.9	$C_8H_6O_2$	1,2-Benzenedicarboxaldehyde	x, y
27	19.1	$C_9H_6O_2$	2H-1-Benzopyran-2-one	x, y
28	22.6	$C_{10}H_6O_3$	2-Hydroxy-1,4-naphthalenedione	x, y
29	40.3	$C_{18}H_{12}$	Benzo[a]anthracene (parental compound)	x, y
30	42.4	$C_{18}H_{10}O_2$	Benzo[a]anthracene-7,12-dione	x, y

The degradation pathway of each PAH can be referred to Fig. 2 provided that all compounds were represented by no. assigned in this table. x: the intermediate identified under reaction condition with 1% acetone. y: the intermediate identified under reaction condition with 16% acetone.

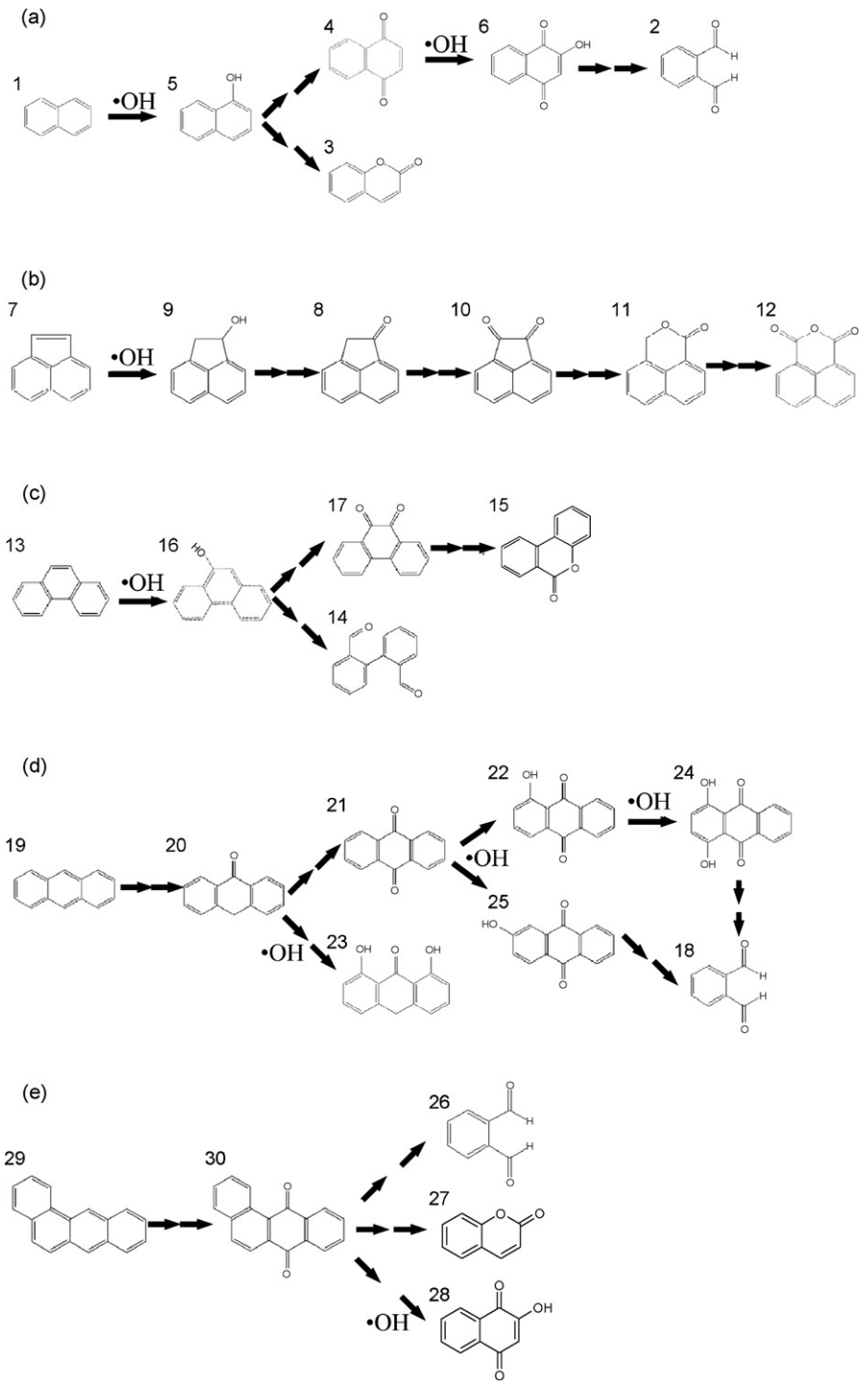

Fig. 2. Proposed degradation pathways of selected PAHs: (a) naphthalene, (b) acenaphthylene, (c) phenanthrene, (d) anthracene and (e) benzo[a]anthracene. The information of each compound can be referred to Table 1 by checking the no. assigned on the left-hand side of their structures.

naphthylene. Although Dewar [8] did not discuss the reactive sites of acenaphthylene, both Klamt [18] and Reisen and Arey [19] agree that the unsaturated bond of the cyclopentafused ring (i.e. the positions 1 and 2) was the major reactive site. Reisen and Arey [19] have further studied reactions of •OH with acenaphthene (Acp) (with a saturated bond of the cyclopentafused ring) and acenaphthylene (Ace) (with an unsaturated bond of the cyclopentafused ring). Their results showed that addition of •OH to the six-membered aromatic rings was the major pathway of degradation of Acp, while for Ace, reaction occurred at the unsaturated bond of the cyclopentafused ring. In their study, some intermediates of Ace produced in the reaction with aromatic rings were found, but none of them were detected in our study.

3.3. Toxicity analysis

Organic compounds can be completely degraded and detoxified into harmless compounds (theoretically, carbon dioxide and water) by photocatalytic oxidation [20,21]. The Microtox® test can be used to assess the acute toxicity of PAHs and their intermediates/degradation products, in order to investigate whether PAHs can be completely detoxified by PCO. Depending on the initial esti-

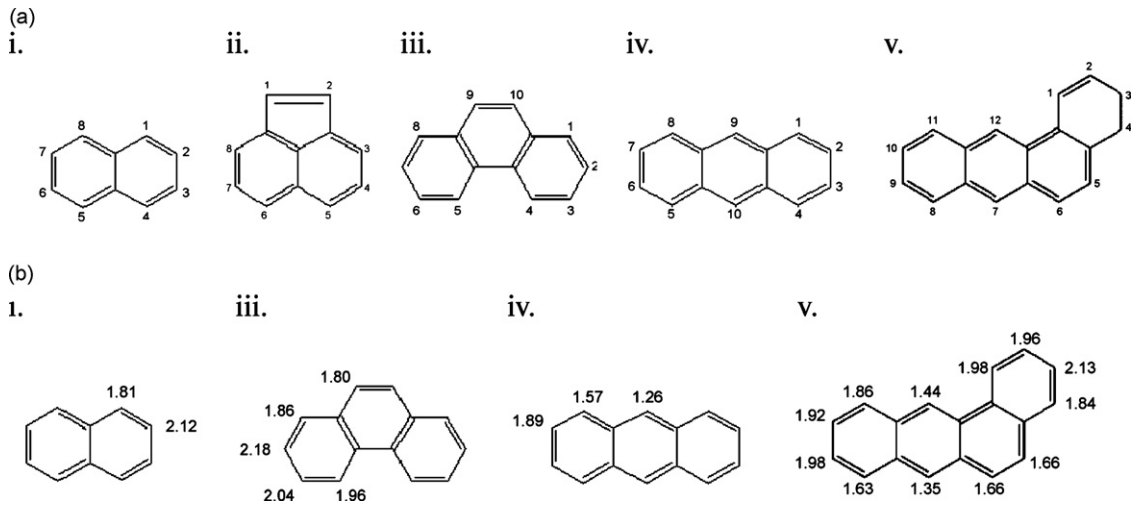

Fig. 3. (a) Numbering and (b) N_u (Dewar) values of selected PAHs: (i) naphthalene, (ii) acenaphthylene, (iii) phenanthrene, (iv) anthracene and (v) benzo[a]anthracene [8].

mation of toxicity of the samples, either the basic test or the 100% test was performed. Results are presented in Table 2 as EC50 values, determined at two exposure times (5 and 15 min), with a 95% confidence interval. A higher EC50 indicates a lower acute toxicity. Also, a smaller 95% confidence interval indicates better quality data than a larger 95% confidence interval.

Since the reaction mixture contained 1% acetone from a PAH stock solution, a control consisting of 1% acetone was conducted in order to monitor acute toxicity caused by acetone itself or intermediates/degradation products generated upon UV irradiation. The results showed that 1% acetone itself did not cause acute toxicity within 15 min of incubation. However, acute toxicity was induced through degradation of acetone upon UV irradiation. Stefan and Bolton [22] studied the degradation pathway of acetone in UV/H_2O_2 process. The degradation system is similar to PCO system as both of them produce hydroxyl radicals to trigger the degradation. The intermediates of acetone degradation included acetic acid and formaldehyde which are highly toxic to the microorganism. Therefore, 24 h was required for the sample to be completely detoxified. In some situations, the EC50 with acetone alone was lower than that of samples containing PAHs and acetone together. This means that the sample containing acetone alone was more toxic. For example, after 14 h of UV irradiation, the EC50–5 min of naphthalene plus acetone was 46.94% while that of acetone alone was 28.97% (Table 2). One possibility is that the degradation pathway for acetone alone is different from degradation of acetone and a PAH. From the results shown in Table 2, only acenaphthylene and phenanthrene showed acute toxicity prior to irradiation. After 1 h irradiation, acute toxicity of some PAHs was induced by the production of intermediates/degradation products, derived either from PAHs or possibly acetone, provided that all selected PAHs were completely degraded within 1 h. This was in agreement with Wernersson et al. [23], that UV can initiate acute toxicity of PAHs by formation of oxidized compounds. However, for acenaphthylene, the EC50–5 min after 1 h irradiation was much higher than that of the original sample. After 15 min incubation, EC50–15 min overlapped that of the original sample. This suggested that time was required for intermediate/degradation products of acenaphthylene to diffuse into the bacterium or to build up to a threshold level for acute toxicity. For all selected PAHs, the EC50 at both exposure times continuously decreased after a minimum 12 h of irradiation. Finally, all of the PAHs which were tested can be completely detoxified within 24 h. In the case of anthracene, only 16 h of irradiation was required for complete detoxification.

Table 2
Results of the Microtox® test samples obtained after PCO degradation of 1% acetone alone and selected PAHs.

Irradiation time (h)	1% acetone alone (control)	
	EC50–5 min (%)	EC50–15 min (%)
(a)		
0	>100	>100
1	69.14 (57.26–83.49)	33.70 (32.77–34.66)
2	36.91 (34.81–39.13)	17.86 (16.05–19.88)
4	47.32 (45.08–49.67)	25.19 (21.27–29.83)
8	27.75 (24.37–31.59)	15.47 (13.29–18.02)
12	21.67 (21.08–22.28)	13.22 (12.37–14.14)
14	28.97 (28.91–29.02)	19.22 (18.44–20.02)
16	42.30 (37.89–47.22)	28.31 (25.37–31.60)
24[a]	>100	>100
Irradiation time (h)	Naphthalene	
	EC50–5 min (%)	EC50–15 min (%)
(b)		
0[a]	>100	>100
1	52.12 (39.00–69.66)	28.75 (25.85–31.98)
2	36.34 (33.57–39.33)	17.72 (16.66–18.86)
4	31.23 (30.21–32.29)	16.08 (15.16–17.05)
8	22.78 (22.04–23.55)	13.06 (12.34–13.83)
12	22.99 (14.37–36.79)	12.54 (10.10–15.57)
14	46.94 (45.32–48.60)	27.12 (26.62–27.62)
16	85.71 (72.83–100.86)	52.08 (48.40–56.04)
Irradiation time (h)	Acenaphthylene	
	EC50–5 min (%)	EC50–15 min (%)
(c)		
0[a]	12.76 (10.25–15.89)	15.64 (14.13–17.31)
1	31.59 (27.33–36.53)	16.64 (16.54–16.73)
2	17.95 (16.88–19.09)	11.08 (10.28–11.95)
4	19.94 (16.83–23.62)	11.30 (9.21–13.87)
8	16.13 (15.03–17.32)	10.49 (10.19–10.80)
12	19.68 (18.98–20.41)	12.79 (12.65–12.92)
14	16.77 (15.45–18.21)	12.10 (10.82–13.52)
16	42.54 (40.62–44.55)	29.86 (28.34–31.46)
24[a]	>100	>100
Irradiation time (h)	Phenanthrene	
	EC50–5 min (%)	EC50–15 min (%)
(d)		
0[a]	30.67 (24.41–38.54)	32.80 (26.54–40.53)
1	25.13 (21.62–29.20)	14.09 (12.58–15.78)
2	24.28 (23.98–24.59)	12.75 (11.02–14.77)
4	26.89 (22.66–31.90)	15.10 (14.65–15.56)
8	29.87 (25.59–34.86)	13.70 (11.62–16.16)

Table 2 (*Continued*)

Irradiation time (h)	Phenanthrene	
	EC50–5 min (%)	EC50–15 min (%)
12	32.51 (30.08–35.14)	16.46 (15.92–17.03)
14	31.68 (29.78–33.69)	17.32 (15.56–19.29)
16	43.36 (41.48–45.33)	26.96 (25.27–28.76)
24	>100	>100
Irradiation time (h)	Anthracene	
	EC50–5 min (%)	EC50–15 min (%)
(e)		
0[a]	>100	>100
1[a]	16.79 (6.30–44.76)	10.21 (4.02–25.88)
2[a]	22.86 (15.82–33.04)	14.36 (13.76–14.99)
4[a]	29.29 (18.93–45.32)	20.03 (16.71–24.00)
8[a]	41.90 (26.16–67.09)	27.96 (21.19–36.88)
16[a]	>100	>100
Irradiation time (h)	Benzo[a]anthracene	
	EC50–5 min (%)	EC50–15 min (%)
(f)		
0	>100	>100
1	30.84 (24.71–38.49)	17.59 (12.12–25.52)
2	22.70 (20.06–25.69)	16.93 (15.26–18.78)
4	39.21 (36.36–42.28)	27.56 (26.54–28.62)
8	43.10 (41.52–44.74)	27.30 (26.60–28.02)
12	61.71 (57.09–66.71)	38.96 (36.49–41.59)
16	57.62 (53.43–62.13)	46.66 (44.62–48.78)
24	>100	>100

Data in parentheses represent 95% confidence range for EC50 values. EC50 > 100 represents non-detectable EC50.

[a] Samples were tested using basic test. For the rest, 100% test was performed.

4. Conclusions

The addition of acetone enhances water solubility of hydrophobic PAHs in aqueous solution and leads to the improvement of PAH degradation. However, the results in this study indicate that the presence of acetone affects the photocatalytic degradation pathway(s). Alcohol, ketone, quinone, aldehydes and benzopyrone were detected in PAH photocatalytic degradation. The intermediates identified in this study were focused on compounds consisting of aromatic rings. Thus, the degradation pathway proposed here may only represent the initial part of the complete degradation pathway. With the addition of a large amount of acetone, higher concentration and more types of intermediates were detected during the PCO degradation of PAHs. Through the intermediates found, the attack on reactive sites by reactive free radicals can be correlated to the localization energies of position of the compound.

For toxicity analysis, only two parental compounds – acenaphthylene and phenanthrene – showed acute toxicity. Irradiation with UV can induce acute toxicity by generation of intermediates/degradation products from PAHs and possibly from acetone. Lastly, all PAHs, especially anthracene, can be completely detoxified within 24 h.

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Appendix A. Percentage yield obtained by some of the intermediates formed during PCO degradation of selected PAHs

PAHs	PCO conditions	Intermediates	Yield (%) obtained at different irradiation time (min)															
			0	2.5	5	10	20	30	40	50	60	90	120	180	210	240	270	300	360
Nap 16% acetone	1% acetone	1,2-Benzenedicarboxaldehyde	0			0	1.6	1.6	2.0	**2.3**	1.3								
		1,4-Naphthalenedione	0			**2.6**	0.9	0.7	0.7	0	0								
	16% acetone	1,2-Benzenedicarboxaldehyde	0	0	2.2	2.0	3.0	3.4		3.7	5.0	6.9	5.4	6.2	**7.2**	5.8	0		
		1,4-Naphthalenedione	0	1.1	1.6	**7.2**	3.2	1.9	1.2		1.0	0.8	0	0	0	0	0	0	
Phe	1% acetone	9,10-Phenanthrenedione	0	0	8.1	10.6	**13.6**	9.7	9.9		8.6	8.5	8.0	0	0	0			
	16% acetone	9,10-Phenanthrenedione	0			18.1	23.3	24.7	**31.3**		15.0	15.7	8.5	8.1		0	0	0	
Ant 16% acetone	1% acetone	1,2-Benzenedicarboxaldehyde	0			2.5	2.9	2.9	**3.0**		2.4	2.0	1.4	0					
		9,10-Anthracenedione	0			25.9	29.8	37.9	**40.3**		33.1	33.2	9.1	1.0					
	16% acetone	1,2-Benzenedicarboxaldehyde	0	1.4	2.8	**3.1**	**3.1**	2.7		2.3	2.7	1.4	2.0	1.7	1.4				
		9,10-Anthracenedione	0	11.3	11.8	**34.2**	13.5	7.4	4.1		2.9	2.0	1.5	1.4	1.2	1.0			
BaA 16% acetone	1% acetone	1,2-Benzenedicarboxaldehyde	0			1.2	1.3	1.6	**2.1**		1.9	1.3	0	0					
		Benzo[a]anthracene-7,12-dione	0			2.3	2.6	**3.0**	1.8		1.0	0	0	0					
	16% acetone	1,2-Benzenedicarboxaldehyde	0			16.4	16.4	17.4	17.2		**21.2**	15.2	13.2	5.6		4.3		2.0	1.5
		Benzo[a]anthracene-7,12-dione	0			15.5	**17.7**	10.4	14.5		5.5	2.6	1.0	0		0		0	0

The bold and underlined number at certain irradiation time was the maximum yield during PCO reaction. Nap: naphthalene; Phe: phenanthrene; Ant: anthracene; BaA: benzo[a]anthracene.

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