Electron-accepting potential of solvents determines photolysis rates of polycyclic aromatic hydrocarbons: Experimental and density functional theory study

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ABSTRACT

Photochemical behaviour of polycyclic aromatic hydrocarbons (PAHs) is strongly dependent on the physical and chemical nature of the media in/on which they exist. To understand the media effects, the photolysis of phenanthrene (PHE) and benzo[a]pyrene (BaP) in several solvents was investigated. Distinct photolysis rate constants for PHE and BaP in the different solvents were observed. Some theoretical parameters reflecting the solvent properties were computed and employed to explain the solvent effects. Acetone competitively absorbed light with PHE and BaP, and the excited acetone molecules played different roles for the photodegradation of PHE and BaP. The photolysis rate constants of PHE and BaP in hexane, isopropanol, ethanol, methanol, acetonitrile and dichloromethane were observed to correlate with the electron-accepting potential of the solvent molecules. Absolute electronegativity of the solvents linearly correlated with the photolytic activity ($\log k$) of the PAHs significantly. The results are important for better understanding the photodegradation mechanism of PAHs in different media.

1. Introduction

Photochemical transformation was an important degradation process for polycyclic aromatic hydrocarbons (PAHs) in the environment [1–5]. PAHs may exhibit apparently different photochemical behaviour in/on different environmental media. The photolysis half-lives ($t_{1/2}$) ranged from a few hours in water to dozens of hours on plants and atmospheric particulates, and to even longer than one thousand hours on fly ash and carbon black [6–11]. The photochemical behaviour of PAHs was highly dependent on the physical and chemical properties of the media in/on which they exist [7,12].

The constituents of environmental media may influence the photodegradation rates of PAHs through competitive light absorption, photosensitization or quenching processes [7,12,13]. Understanding the properties of the media that have impacts on the degradation rates of PAHs, however, is very complicated due to the uncertain compositions of the media. Therefore, some simplified chemical model systems, such as organic solvents, have been used to study the media effects on the photodegradation process [14,15]. Most of these studies have shown that the photolysis rates of PAHs are dependent on the nature of solvents [16–20].

A general standpoint of the solvent effects on the photolysis of PAHs is that the degradation of PAHs is fast in polar solvents [16,20]. However, it is not easy to define polarity of solvent precisely, and it is even more difficult to assess it quantitatively [21]. Moeini-Nombel and Matsuzawa [17] suggested that photodegradation rates of PAHs were strongly related to the solubility of oxygen in solvents. However, some other studies found that oxygen concentration had minor or opposite effects on the photodegradation rates of PAHs in solutions [22,23]. Besides oxygen molecules, solvent molecules (such as cyclohexane) were also involved in the photolysis process of PAHs [24]. Therefore, further studies are necessary for understanding solvent effects on the photolysis of PAHs.

Solvent influences the chemical reactions as either a continuum medium or individual molecules [21,25,26]. Theoretical methods have been proven to be important to understand the solvent effects from microscopic structures [25]. In this study, a combined experimental and density functional theory (DFT) computational method was used to illustrate the solvent effects on the photolysis of PAHs. The photolysis kinetics of phenanthrene (PHE) and benzo[a]pyrene (BaP) dissolved in methanol, ethanol, isopropanol, acetone, acetonitrile, hexane, and dichloromethane (DCM) was investigated. These solvents were selected as they were used to model the constituents of the environmental media like plant waxes [15]. Molecular structural parameters reflecting the solvent effects were computed. Based on the photolysis rate constants and the solvent property parameters, the effects of light absorption,

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dipolarity/polarizability and electron-accepting (donating) potential of the solvents on the photolysis of the PAHs were discussed.

2. Materials and methods

2.1. Chemicals

PHE (98% purity) was purchased from TCI (Tokyo, Japan) and BaP (96.5% purity) from ACROS (New Jersey, USA). Acetonitrile, hexane, acetone, isopropanol, ethanol, methanol and DCM were chromatographic grade and supplied by TEDIA (Fairfield, USA).

2.2. Photolysis experiments

Photolysis solutions of PHE and BaP were prepared using the different solvents. An XPA-1 merry-go-round photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China) with a 300-W high pressure mercury arc lamp was used for the photodegradation experiments. The light irradiance spectrum was measured by a monochromator (Acton, SP-300). Samples were irradiated in the quartz test tubes and aliquots were taken from the illuminated reactor at selected time intervals. The experiments were carried out in triplicate. Dark control experiments in the corresponding solvents were conducted concurrently at the identical conditions.

2.3. Analytical methods

The PAHs were analyzed by an Agilent 1100 HPLC system equipped with a G1321A fluorescence detector and a Supelcosil LC-PAH column (250 mm × 4.6 mm i.d., 5 μm particle size, Supelco). For the analysis of the PAHs dissolved in hexane and DCM, the solvents were replaced by acetonitrile through evaporation and redissolution prior to injection to the HPLC. The mobile phase was acetonitrile with a flow rate of $1\,\mathrm{mL\,min^{-1}}$. The concentrations of PHE and BaP were determined on the basis of peak area quantification. The excitation wavelengths were 250 nm and 260 nm for PHE and BaP, and the emission wavelengths were 366 nm and 406 nm, respectively. UV–vis absorption spectra and fluorescence spectra of the PAHs in the different solvents were measured with a Hitachi UV2800 spectrophotometer and a Hitachi F4500 fluorescence spectrophotometer, respectively.

2.4. Molecular parameters and computational methods

Ionization potential (IP), electron affinity (EA) and absolute electronegativity (χ) were selected to characterise the electron-donating and -accepting potential for the chemicals [27,28]. IP and EA were computed using the difference of separate self-consistent field (SCF) energies of the neutral and corresponding anionic and cationic systems [29]. When IP and EA were obtained,

χ was calculated using $\chi = 1/2(IP + EA)$ [27,30,31]. EA of the excited state molecules (EA_{T1}) was calculated using $EA_{T1} = EA - E_T$, with E_{T1} standing for the lowest triplet excitation energy. Dipolarity/polarizability parameter (π^*) was a measurement of solvent's ability to stabilize a charge or a dipole by virtue of its dielectric effect, and the data were taken from Kamlet et al. [32].

DFT calculations were performed employing Gaussian 03 software package [33]. The geometries of the chemicals were optimized using the hybrid density functional B3LYP method with the 6-31 + G(d) basis set and then confirmed by the frequency analysis. The single-point and the lowest triplet excitation energy were calculated at B3LYP/6-31 + G(d) level. The self-consistent reaction field (SCRF) method with polarizable continuum model (PCM) was used to consider the properties of the PAH molecules in the solvents.

3. Results and discussion

3.1. Photolysis rates of the PAHs in the different solvents

All the experiments carried out in the dark showed negligible degradation for the PAHs. The photolysis of the PAHs in the solvents was observed to follow the first order kinetics (Fig. 1). The photolysis rate constants (k) were derived from the slope of $\ln(C/C_0)$ versus t. For PHE or BaP, the k values are different in the diverse solvents. The k of BaP in DCM was larger than in hexane with a factor of 24, and the k of PHE in DCM was larger than in acetone with a factor of 36 (Table 1). For PHE, the photolysis rate in acetone was the slowest. However, the photolysis rate of BaP in acetone was faster than in the other solvents except for DCM and acetonitrile (Table 1).

In the other solvents except for acetone, the trends of k variation with the kind of solvents for the two PAHs are similar (Table 1). Both PHE and BaP degraded faster in DCM than in acetonitrile, which was consistent with the results of Lehto et al. [18]. In methanol, the photolysis of both PHE and BaP was faster than in hexane, whereas their photolysis was slower than that in DCM.

3.2. Light-absorbing effects of acetone on the PAHs photolysis

Acetone significantly inhibited the photolysis rate of PHE, but enhanced the photolysis of BaP (Table 1). Acetone has much stronger light absorption than PHE and BaP (Fig. 2). Therefore, acetone competitively absorbs light with PHE and BaP. However, the excited acetone molecules could play different roles for the photodegradation of PHE and BaP. The electron affinity of electronically excited state acetone (acetone*) was calculated to be $EA_{T1} = -5.21\,\mathrm{eV}$, and the ionization potential for the ground state BaP was $IP = 5.18\,\mathrm{eV}$. As $\Delta G = EA_{T1}(\mathrm{acetone^*}) + IP(\mathrm{BaP}) < 0$, the transfer of electrons from BaP to acetone* is viable, which may facilitate the photodegradation of BaP. However, $IP = 5.92\,\mathrm{eV}$ for PHE, and the corresponding $\Delta G > 0$. Thus, the transfer of electrons from PHE to
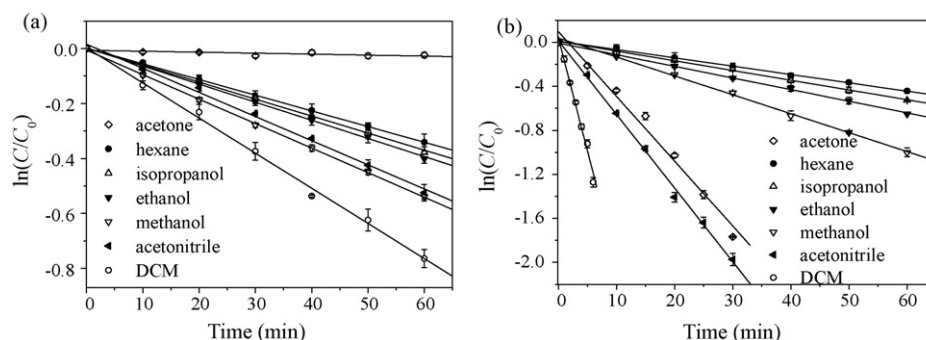

Fig. 1. Photolysis kinetics of (a) PHE and (b) BaP in 7 solvents under 300-W mercury lamp.

Table 1
Photolysis rate constants (k) of PHE and BaP in the studied solvents and some solvent property parameters (π^*, EA, IP, χ).

No.	Solvent	k_{PHE} (10^{-3} min^{-1})	k_{BaP} (10^{-3} min^{-1})	π^{*a}	EA (eV)	IP (eV)	χ (eV)
1	Hexane	5.71 ± 0.05	8.44 ± 0.002	−0.08	−1.39	9.71	4.16
2	Isopropanol	6.21 ± 0.02	8.85 ± 0.06	0.48	−1.25	9.82	4.29
3	Ethanol	6.59 ± 0.02	9.07 ± 0.03	0.54	−1.36	10.18	4.41
4	Methanol	8.92 ± 0.13	17.22 ± 0.75	0.6	−1.44	10.67	4.62
5	Acetonitrile	8.78 ± 0.06	67.12 ± 1.17	0.75	−1.03	11.84	5.41
6	DCM	12.79 ± 0.01	206.31 ± 1.80	0.82	0.52	11.05	5.79
7	Acetone	0.36 ± 0.01	58.87 ± 0.89	–	–	–	–

[a] From Kamlet et al. [32].
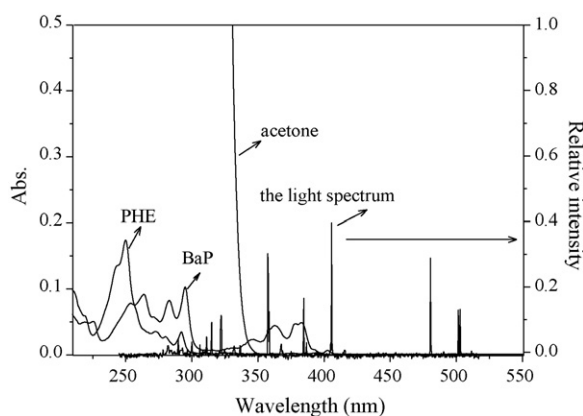
Fig. 2. UV–vis absorption spectra of PHE and BaP (0.4 mg L^{-1} in methanol), acetone and the relative light irradiance.

acetone* is not theoretically favorable, which may inhibit the photodegradation of PHE. For the studied solvents, only acetone had an obvious light absorption at the experimental light wavelengths. Thus, the photolysis in acetone was excluded from the discussions below.

3.3. Dipolarity/polarizability role of the solvents as continuum media on the PAHs photolysis

As shown in Table 1, the photolysis rate constants of PHE and BaP in hexane, methanol, acetonitrile and DCM increased with π^*. This is consistent with the commonly proposed standpoint that the solvent polarity influences PAHs photolysis [16,20,34]. π^* evaluates the ability of the solvent to stabilize a charge by its dielectric effect. The solvent with a large π^* value may facilitate the stabilization and separation of charge transfer state of PAH molecules and hence the photolysis. However, no quantitative relations between π^* and the photolytic activity ($\log k$) of the two PAHs were observed, when more solvents were taken into consideration (Fig. 3), indicating that
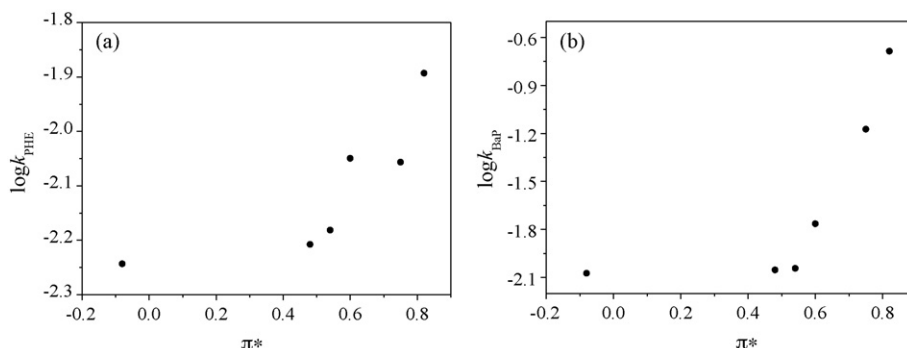
the solvent dipolarity/polarizability did not play a decisive role on the photolysis rate of the PAHs.

3.4. Electron-accepting potential of the solvent molecules on photolysis of the PAHs

The computed IP values of the excited state PAHs (PAHs*) in the studied solvents ranged from 3.14 eV to 3.18 eV for the excited state PHE and 3.43 eV to 3.46 eV for the excited state BaP. IP reflects the electron-donating tendency. The IP values of the two PAHs* were smaller than those of the studied solvents (with $IP > 9.6$ eV, shown in Table 1), implying that the PAHs* are electron donors. Some previous studies [34–36] also indicated that photoinduced electron transfer is a possible photodegradation path of PAHs. Therefore, the solvents could be involved in the photodegradation process as electron acceptors.

The electron affinity (EA) and absolute electronegativity (χ) values that reflect the electron-accepting potential of the solvents are listed in Table 1. The $\log k$ values of both PHE and BaP in hexane, ethanol, acetonitirle, and DCM increased with EA (Table 1). Meanwhile, a significant linear relationship was observed between $\log k$ of the two PAHs and χ, for which the correlation coefficients (r) are larger than 0.91 (Fig. 4). χ measures the tendency of a molecule to attract electrons. Solvent molecule with high χ may get electron more easily than that with low χ. The results prove the vital role of electron-accepting potential of the solvents in the photolysis reaction of the PAHs.

Besides solvent molecules, dioxygen (O_2) may also be an electron acceptor in the photolysis process of PAHs. As O_2 molecules are non-polar, the solubility of O_2 in hexane usually is higher than in methanol [37]. However, the photodegradation of the PAHs was slower in hexane than in methanol (Table 1). Furthermore, the removal of O_2 by N_2 purge did not change the photolysis rate constants of PHE and BaP obviously (Fig. 5), indicating that the influence of O_2 was minor in this investigation. Thus, the solvent molecules mainly act as electron acceptors to influence the photolysis rates of PAHs.

Fig. 3. Plots of the photolytic activity ($\log k$) versus dipolarity/polarizability (π^*) of the solvents for (a) PHE and (b) BaP.
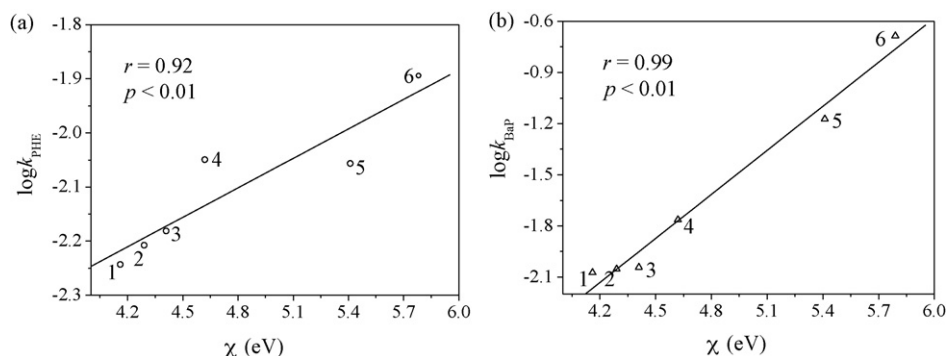
Fig. 4. Correlations of absolute electronegativity (χ) of the solvents and the photolytic reactivity ($\log k$) for (a) PHE and (b) BaP.
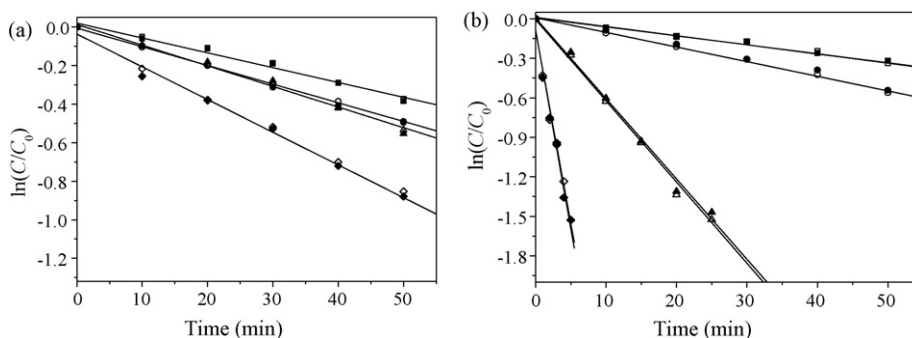

Fig. 5. Photolysis kinetics of (a) PHE and (b) BaP in methanol ($\bigcirc$), nitrogen-purged methanol ($\bullet$), acetonitrile ($\blacktriangle$), nitrogen-purged acetonetrile ($\triangle$), hexane ($\square$), nitrogen-purged hexane ($\blacksquare$), DCM ($\lozenge$) and nitrogen-purged DCM ($\blacklozenge$).

4. Conclusions

Different photolysis rate constants for PHE and BaP in the diverse solvents were observed. Acetone competitively absorbed light with PHE and BaP molecules, while the excited acetone molecules played opposite roles on their photodegradation kinetics. The photolysis rate constants of PHE and BaP in hexane, isopropanol, ethanol, methanol, acetonitrile and DCM were mainly influenced by electron-accepting potential of the solvents. The photolytic activity ($\log k$) of the two PAHs positively correlates with χ significantly. As only a limited number of solvents were included in the study, further investigations should extend the number and representativeness of solvents so as to well model the properties of environmental media.

Acknowledgements

References

[1] R.F. Lee, W.S. Gardner, J.W. Anderson, J.W. Blaylock, J. Barwell-Clarke, Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures, Environ. Sci. Technol. 12 (1978) 832–838.
[2] J. Kochany, R.J. Maguire, Abiotic transformations of polynuclear aromatic hydrocarbons and polynuclear aromatic nitrogen heterocycles in aquatic environments, Sci. Total Environ. 144 (1994) 17–31.
[3] J.F. Niu, J.W. Chen, D. Martens, B. Henkelmann, X. Quan, F.L. Yang, H.K. Seidlitz, K.-W. Schramm, The role of UV-B on the degradation of PCDD/Fs and PAHs sorbed on surfaces of spruce (Picea abies (L.) Karst.) needles, Sci. Total Environ. 322 (2004) 231–241.
[4] F.J. Rivas, F.J. Beltran, B. Acedo, Chemical and photochemical degradation of acenaphthylene. Intermediate identification, J. Hazard. Mater. 75 (2000) 89–98.
[5] L.H. Zhang, P.J. Li, Z.Q. Gong, X.M. Li, Photocatalytic degradation of polycyclic aromatic hydrocarbons on soil surfaces using TiO₂ under UV light, J. Hazard. Mater. 158 (2008) 478–484.
[6] T.D. Behymer, R.A. Hites, Photolysis of polycyclic aromatic hydrocarbons adsorbed on simulated atmospheric particulates, Environ. Sci. Technol. 19 (1985) 1004–1006.
[7] T.D. Behymer, R.A. Hites, Photolysis of polycyclic aromatic hydrocarbons adsorbed on fly ash, Environ. Sci. Technol. 22 (1988) 1311–1319.
[8] J.S. Miller, D. Olejnik, Photolysis of polycyclic aromatic hydrocarbons in water, Water Res. 35 (2001) 233–243.
[9] M.P. Fasnacht, N.V. Blough, Aqueous photodegradation of polycyclic aromatic hydrocarbons, Environ. Sci. Technol. 36 (2002) 4364–4369.
[10] J.F. Niu, J.W. Chen, D. Martens, X. Quan, F.L. Yang, A. Kettrup, K.-W. Schramm, Photolysis of polycyclic aromatic hydrocarbons adsorbed on spruce [Picea abies (L.) Karst.] needles under sunlight irradiation, Environ. Pollut. 123 (2003) 39–45.
[11] D.G. Wang, J.W. Chen, Z. Xu, X.L. Qiao, L.P. Huang, Disappearance of polycyclic aromatic hydrocarbons sorbed on surfaces of pine [Pinua thunbergii] needles under irradiation of sunlight: volatilization and photolysis, Atmos. Environ. 39 (2005) 4583–4591.
[12] J.R. Odum, S.R. McDow, R.M. Kamens, Mechanistic and kinetic studies of the photodegradation of benz[a]anthracene in the presence of methoxyphenols, Environ. Sci. Technol. 28 (1994) 1285–1290.
[13] M. Jang, S.R. McDow, Benz[a]anthracene photodegradation in the presence of known organic constituents of atmospheric aerosols, Environ. Sci. Technol. 29 (1995) 2654–2660.
[14] A. Feilberg, T. Nielsen, Photodegradation of nitro-PAHs in viscous organic media used as models of organic aerosols, Environ. Sci. Technol. 35 (2001) 108–113.
[15] T. Katagi, Photodegradation of pesticides on plant and soil surface, Rev. Environ. Contam. Toxicol. 182 (2004) 1–195.
[16] G.K.-C. Low, G.E. Batley, C.I. Brockbank, Solvent-induced photodegradation as a source of error in the analysis of polycyclic aromatic hydrocarbons, J. Chromatogr. 392 (1987) 199–210.
[17] L. Moeini-Nombel, S. Matsuzawa, Effect of solvents and a substituent group on photooxidation of fluorine, J. Photochem. Photobiol. A 119 (1998) 15–23.
[18] K.-M. Lehto, H. Lemmetyinen, J. Puhakka, Photodegradation of selected aromatic constituents of creosote in organic solvents, Polycyclic Aromat. Compd. 21 (2000) 297–309.
[19] K.-W. Agata, D. Dąbrowska, J. Namieśnik, Photodegradation and biodegradation study of benzo(a)pyrene in different liquid media, J. Photochem. Photobiol. A 168 (2004) 109–115.
[20] O. Cvrčková, M. Ciganek, Photostability of polycyclic aromatic hydrocarbons (PAHs) and nitrated polycyclic aromatic hydrocarbons (NPAHs) in dichloromethane and isooctane solutions, Polycyclic Aromat. Compd. 25 (2005) 141–156.

[21] C. Reichardt, Pyridinium N-phenolate betaine dyes as empirical indicators of solvent polarity: some new findings, Pure Appl. Chem. 76 (2004) 1903–1919.

[22] Y.P. Sun, B. Ma, G.E. Lawson, C.E. Bunker, H.W. Rollins, Effect of photochemical reaction of pyrene in alcohol and aqueous solvent systems on spectroscopic analyses, Anal. Chim. Acta 319 (1996) 379–386.

[23] K.-M. Lehto, E. Vuorimaa, H. Lemmetyinen, Photolysis of polycyclic aromatic hydrocarbons (PAHs) in dilute aqueous solutions detected by fluorescence, J. Photochem. Photobiol. A 136 (2000) 53–60.

[24] M. Lamotte, J. Pereyre, R. Lapouyade, J. Joussot-Dubien, Multiphotonic photolysis of perylene and pyrene in liquid cyclohexane, J. Photochem. Photobiol. A 58 (1991) 225–237.

[25] C.J. Cramer, D.G. Truhlar, Implicit salvation models: equilibria, structure, spectra, and dynamics, Chem. Rev. 99 (1999) 2161–2200.

[26] A. Liu, D.M. Loffredo, A.D. Trifunac, Photoionization and ensuing ion-molecule reactions of polycyclic aromatic hydrocarbons in alkane and alcohol solutions, J. Phys. Chem. 97 (1993) 3791–3799.

[27] R.G. Parr, R.G. Pearson, Absolute hardness: companion parameter to absolute electronegativity, J. Am. Chem. Soc. 105 (1983) 7512–7516.

[28] J. Choi, W. Choi, B.J. Mhin, Solvent-specific photolytic behavior of octachlorodibenzo-p-dioxin, Environ. Sci. Technol. 38 (2004) 2082–2088.

[29] C.M. Chang, DFT-based linear solvation energy relationships for the infrared spectral shifts of acetone in polar and nonpolar organic solvents, J. Phys. Chem. A 112 (2008) 2482–2488.

[30] R. Parthasarathi, V. Subramanian, D.R. Roy, P.K. Chattaraj, Electrophilicity index as a possible descriptor of biological activity, Bioorg. Med. Chem. 12 (2004) 5533–5543.

[31] P. Chaquin, Absolute electronegativity and hardness: an analogy with classical electrostatics suggests an interpretation of the Parr 'electrophilicity index' as a 'global energy index' leading to the 'minimum electrophilicity principle', Chem. Phys. Lett. 458 (2008) 231–234.

[32] M.J. Kamlet, J.-L.M. Abboud, M.H. Abraham, R.W. Taft, Linear solvation energy relationships. 23. A comprehensive collection of the solvatochromic parameters, π^*, α, and β, and some methods for simplifying the generalized solvatochromic equation, J. Org. Chem. 48 (1983) 2877–2887.

[33] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2003.

[34] M.E. Sigman, P.F. Schuler, M.M. Ghosh, R.T. Dabestani, Mechanism of pyrene photochemical oxidation in aqueous and surfactant solutions, Environ. Sci. Technol. 32 (1998) 3980–3985.

[35] M.P. Fasnacht, N.V. Blough, Mechanisms of the aqueous photodegradation of polycyclic aromatic hydrocarbons, Environ. Sci. Technol. 37 (2003) 5767–5772.

[36] S. Fioressi, R. Arce, Excited states and intermediate species of benzo[e]pyrene photolyzed in solution and adsorbed on surfaces, J. Phys. Chem. A 107 (2003) 5968–5975.

[37] S.R. Bakalyar, M.P.T. Bradley, R. Honganen, The role of dissolved gases in high-performance liquid chromatography, J. Chromatogr. 158 (1978) 277–293.