ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 119 (1998) 15–23

Journal of Photochemistry and Photobiology A:Chemistry

Effect of solvents and a substituent group on photooxidation of fluorene

Leila Moeini-Nombel, Sadao Matsuzawa*

National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

Received 20 November 1997; received in revised form 27 August 1998; accepted 2 September 1998

Abstract

The effect of solvents and a substituent group on photooxidation of fluorene was investigated. Solutions of fluorene and its derivatives ($c = 0.25$ g l^{-1}) were irradiated using artificial light from a xenon lamp (100 mW/cm^2) and degradation (%), rate constants (k_p), quantum yields (Φ) and half-lives ($t_{1/2}$) were compared. In addition, reaction products formed in each case were analyzed and compared with those of fluorene. Photodegradation (%) for fluorene varied depending on the solvent used. Dichloromethane gave the largest rate constant (3.4×10^{-4} s^{-1}) and quantum yield (0.009). Both values decreased in the order of dichloromethane > acetonitrile > methanol > acetonitrile/water (70/30) > acetonitrile/water(50/50). The relation between the solubility of oxygen in solvent and the reactivity is described. 1-methylfluorene exhibited comparable photostability to that of fluorene, while 2-nitrofluorene showed good photostability. In case of 2-nitrofluorene, direct oxidation scarcely occurred and a replacement reaction was induced by the presence of a chlorine source. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Fluorene; Photooxidation; Photodegredation; Polycyclic aromatic hydrocarbon; PAH

1. Introduction

The presence of toxic polycyclic aromatic hydrocarbons (PAHs) in the environment is worldwide and their atmospheric fate has received considerable attention [1–3] since PAHs transform and increase the toxicity.

Fluorene, a three-ring aromatic hydrocarbon, has been known as a toxic and important pollutant in ecosystem. Hence the US Environmental Protection Agency designated it as one of priority pollutants. Fluorene and its derivatives have been found in the air as vapor [4–6] and an adsorbate on particulate matters [7]. These mostly originate from anthropogenic sources. One major emission source are automobiles. It has been reported that fluorene [8], 9-fluorenone and alkylfluorenones [9] are emitted from diesel and gasoline-powered engines. Automobiles with no catalytic converters showed the highest emission rates and highest concentrations of the pollutant. A part of emitted fluorene travels far from the emission sources. However, the majority of it accumulates on the ground due to rain [6] or atmospheric particulates [5–7,10] and remains in the soil, water, plants, etc. Ligocki et al. detected fluorene and 9-fluorenone in rainwater [6]. Deposition of fluorene and alkylated fluorene in seawater at Massachusetts Bay has been reported by Golomb et al. [10]. In addition, several researchers have reported that fluorene predominates in sediment, fish and plant [11,12] indicating its stable nature in the environment. Under irradiation of light and in the presence of NO_x, fluorene can be nitrated and transformed to mutagenic compounds such as 1-, 2-, 3- and 4-nitrofluorenes. Furthermore, 9-fluorenone which is more toxic than the parent PAH is formed as a main product [5]. Although high stability and long half-life under light have been reported for fluorene by Behymer et al. [13], this compound thus increases its toxicity under a specific condition.

As described above, many researchers pointed out fluorene and its derivatives as a group of significant environmental pollutants, but little is known about photochemical reaction of these compounds. Although Barbas et al. recently investigated photochemistry of fluorene at a silica gel/air interface [14], fundamental research is still required, particularly for a better understanding of the degradation mechanism. Consequently, we have undertaken a study on factors which affect photodegradation of fluorenes. Here we report on the effect of solvents and a substituent group.

---

*Corresponding author. Tel.: +81-298-58-8262; fax: +81-298-58-8258; e-mail: sadao@nire.go.jp

PII: S1010-6030(98)00391-8

2. Experimental

Stock solutions (0.25 g l^{-1}) of fluorene ((**I**) in Fig. 1), 1-methylfluorene (**III**), 2-nitrofluorene (**V**), 9-fluorenecarboxylic acid (**VIII**) and 9-fluoreneacetic acid (**IX**) in dichloromethane (DCM) and acetonitrile (ACCN) were prepared and 0.5 ml of each solution was irradiated to obtain kinetic data (2 ml was irradiated for identification of degradation products). Methanol (MeOH) and mixtures of ACCN and water (H_2O) (70 : 30 and 50 : 50) were also used as solvents in case of fluorene. Compounds used as reactants were all of analytical grade (purity: >98%) purchased from Aldrich. *o*-Nitrobenzaldehyde used for actinometry was purchased from Tokyo Kasei and used as received (purity: >98%).

A sample solution taken in a glass vessel was placed in a chamber and was irradiated for several hours under light from a xenon lamp (100 mW/cm^2). In order to adjust the energy distribution similar to that of solar radiation, the light was passed through an AM-1.5 filter. Furthermore, heat inherent in the light was removed by passing it through a water filter with 5 mm thickness. Photoirradiation was carried out at room temperature under air atmosphere.

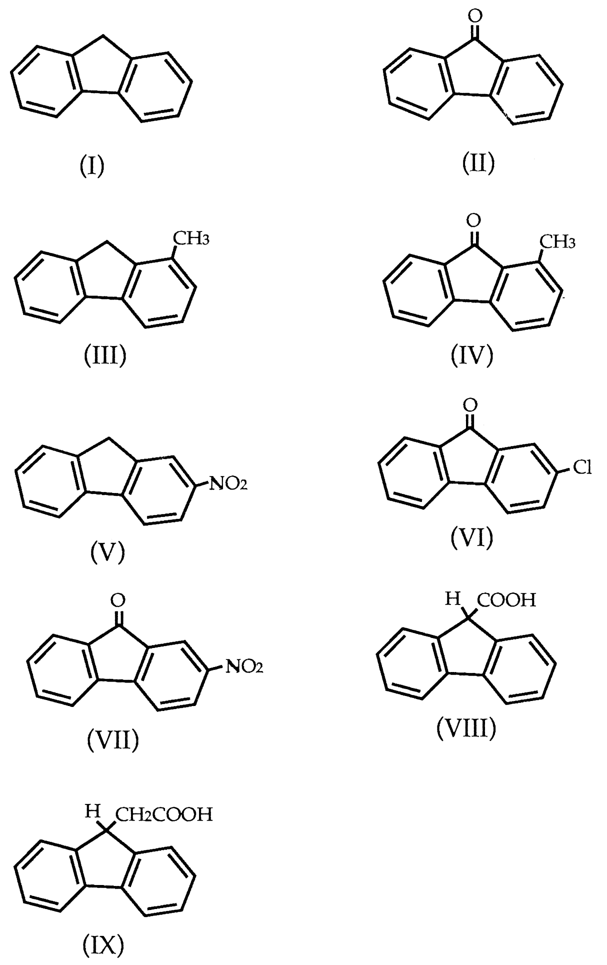

Fig. 1. Structure of reactants and identified reaction products.

Determination of quantum yields (Φ) for fluorene, 1-methylfluorene and 2-nitrofluorene was performed based on a method reported by Mill et al. [15]. When a substrate is irradiated with polychromic light such as solar light and/or artificial light from a xenon lamp, wavelength-averaged quantum yields have to be principally determined by measuring irradiance and the molar extinction coefficient of the substrate for each wavelength as described by Zepp [16] and Draper [17]. However, we determined the quantum yield at a specific wavelength (299 nm) since fluorene and methylfluorene show absorption in a very narrow wavelength range (295–305 nm) of the incident light and the reactivity for 2-nitrofluorene, of which absorption spectrum ranges to 400 nm, under our experimental condition was very low. Actinometry was performed using 10^{-3}–10^{-4} M ACCN solutions of *o*-nitrobenzaldehyde ($\Phi = 0.505$). In quantum yield measurements, a solution for actinometry was simultaneously irradiated with sample solutions. The incident light intensity (I_0) obtained by this method was 1.366×10^{-6} Einstein $l^{-1}\,s^{-1}$ (this value corresponds to 8.23×10^{17} photons $l^{-1}\,s^{-1}$). The rate constants for apparent consumption of fluorene and its derivatives were obtained from the relation

$$-\ln\left(\frac{C_t}{C_0}\right) = k_{\mathrm{p}}t \qquad (1)$$

where C_0 and C_t are the concentrations (M) of substrate at times zero and t (s), k_{p} is the first-order rate constant (s^{-1}). Using I_0 and k_{p} obtained from the relation for each compound, the quantum yield (Φ) was calculated using the following equation

$$\Phi = \frac{k_p}{2.3\varepsilon I_0 r} \qquad (2)$$

where ε is the molar extinction coefficient ($M^{-1}\,cm^{-1}$) and r (cm) is the reactor constant. The ε values measured at 299 nm for *o*-nitrobenzaldehyde, fluorene, 1-methylfluorene and 2-nitrofluorene were 2760, 11 300, 8100 and 23 100, respectively. r was assumed to be 1.0 in this study. Half-lives $t_{1/2}$ (s) were also calculated using Eq. (3) which was derived from Eq. (1) by replacing C_t with $C_0/2$.

$$t_{1/2} = \frac{0.693}{k_p} \qquad (3)$$

Analysis of reactants and reaction products was performed with a combined chromatographic and spectroscopic method. Gas chromatography/mass spectrometry (GC/MS) analysis was mainly applied to quantitative and qualitative measurements. Quantification was carried out by the internal standard method. GC and MS detectors used were HP 5890 series II and HP 5971, respectively. Conditions for GC/MS analysis were as follows. Column: HP-1 or HP-5 (0.2 mm i.d. × 25 m); carrier gas and flow rate, He, 1 ml min^{-1}; injection temperature, 200°C; oven temperature, 70–210°C programmed at 7°C min^{-1}. In addition to GC/MS, HPLC analysis using a reversed phase C18 column and photodiode array absorbance (Shimazu SPD-M6A) and fluorescence (Hitachi F1000) detectors was conducted to increase the reliability of the identification for degradation products. A mixture of ACCN and H_2O (74/26) was used as a mobile phase for HPLC. In some cases, GC/MS/MS (Finigan Mat GCQ) was also applied to increase confidence of the identification. 9-Fluorenone, 2-fluorenecarbaldehyde and benzo[c]cinnoline used for comparison of spectra were of analytical grade (purity: >98%) purchased from Aldrich and Tokyo Kasei.

3. Results

3.1. Comparison of reactivity

Fig. 2 shows dependence of degradation (%), which was calculated using the following equation: $[(C_0-C_t)/C_0] \times 100$, for fluorene on the kind of solvent. The data obtained for ACCN solutions are indicated with open circles. From the curves shown in Fig. 2, it is apparent that DCM gives higher degradation (%) than MeOH and ACCN, and two mixtures of ACCN and H_2O give lower values. Upon 2 h of irradiation, degradation for DCM solution is 86%, although those for MeOH and ACCN solutions are 63% and 44%, respectively. Increasing H_2O content in ACCN decreases the reactivity. Upon 2 h of irradiation, degradation in ACCN/H_2O (50/50) solution is only 1%. At 6 h, fluorene is mostly degraded in DCM and ACCN, but 7% of substrate remained in MeOH solution. Mixtures of ACCN and H_2O showed gradual increase in degradation (%) with increasing irradiation time, however, values obtained at 6 h are relatively low: 67% in ACCN/H_2O (70/30) and 25% in ACCN/H_2O (50/50). The regression $-\ln(C_t/C_0)$ vs. time, shown in Fig. 3 clearly exhibits these differences in the reactivity. Rate constants, quantum yields, and half-lives obtained for reaction of fluorene in this study are given in Table 1. DCM gave the largest rate constant (3.4×10^{-4}) and quantum yield (0.009). The quantum yield decreases in the order of DCM > ACCN > MeOH > ACCN/H_2O(70/30) > ACCN/H_2O(50/50). The half-life in DCM was below one hour ($t_{1/2} = 0.57$).

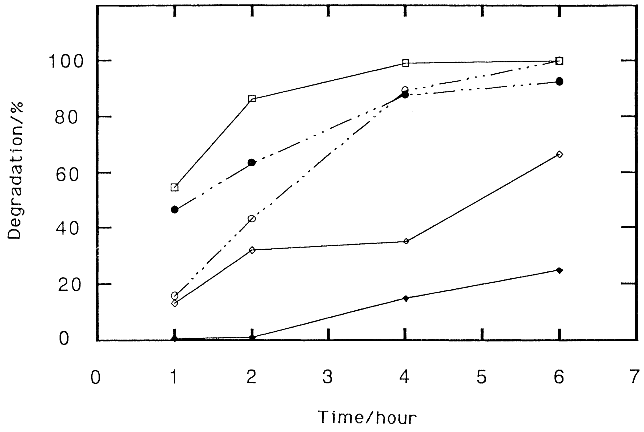

Fig. 2. Dependence of photodegradation (%) of fluorene on the kind of solvent —⊟—, dichloromethane (DCM); —●- - -, methanol (MeOH); —○- - -, acetonitrile (ACCN); —◇—, acetonitrile (ACCN)/water (H_2O) (70/30); —◆—, acetonitrile (ACCN)/water (H_2O) (50/50).

Fig. 4 shows the effect of substituent group on photodegradation (%) of fluorene. 1-Methylfluorene and 2-nitrofluorene were used as substrates for comparison and ACCN was used as a solvent. The data obtained for an ACCN solution of fluorene is also given in Fig. 4. Upon 2 h of irradiation, degradation for 1-methylfluorene approaches about 74%, while that for fluorene is about 44%. Initially 1-methylfluorene is more degradable than fluorene. On the other hand, upon 2 h of irradiation, 2-nitrofluorene shows no photodegradation. Upon 4 h of irradiation, degradation (%) of both fluorene and 1-methylfluorene increases and, at 6 h, approaches 100%. In contrast, degradation for 2-nitrofluorene remains below 10%. First-order rate constants estimated from the regression $-\ln(C_t/C_0)$ vs. time (h), shown in Fig. 5, and quantum yields obtained for 1-methylfluorene and 2-nitrofluorene are also included in Table 1. As for fluorene and the two substituted fluorenes studied here, the rate constants (s^{-1}) observed on ACCN solutions ranged from 9.16×10^{-6} for 2-nitrofluorene to 1.8×10^{-4} for 1-methylfluorene. On the other hand, quantum yield on ACCN solution varied from 0.0001 for 2-nitrofluorene to 0.007 for 1-methylfluorene. Half-lives (h) calculated using Eq. (3) are

Table 1
Rate constants, quantum yields and half-lives for photooxidation of fluorene and its derivatives

Solvent	Substrate	k (s^{-1})	$t_{1/2}$ (h)	Quantum yield (Φ)
MeOH	Fluorene	1.1×10^{-4}	1.75	0.003
DCM	Fluorene	3.4×10^{-4}	0.57	0.009
ACCN	Fluorene	1.3×10^{-4}	1.48	0.004
ACCN/H_2O (70/30)	Fluorene	2.9×10^{-5}	6.64	0.0008
ACCN/H_2O (50/50)	Fluorene	2.4×10^{-5}	8.02	0.0006
ACCN	2-nitro-fluorene	9.16×10^{-6}	21.01	0.0001
DCM	2-nitro-fluorene	1.7×10^{-4}	1.13	0.002
ACCN	1-methyl-fluorene	1.8×10^{-4}	1.07	0.007
DCM	1-methyl-fluorene	2.1×10^{-4}	0.92	0.008

MeOH: methanol; DCM: dichloromethane; ACCN: acetonitrile.
$t_{1/2}$: values obtained in seconds were converted to the unit of hour.

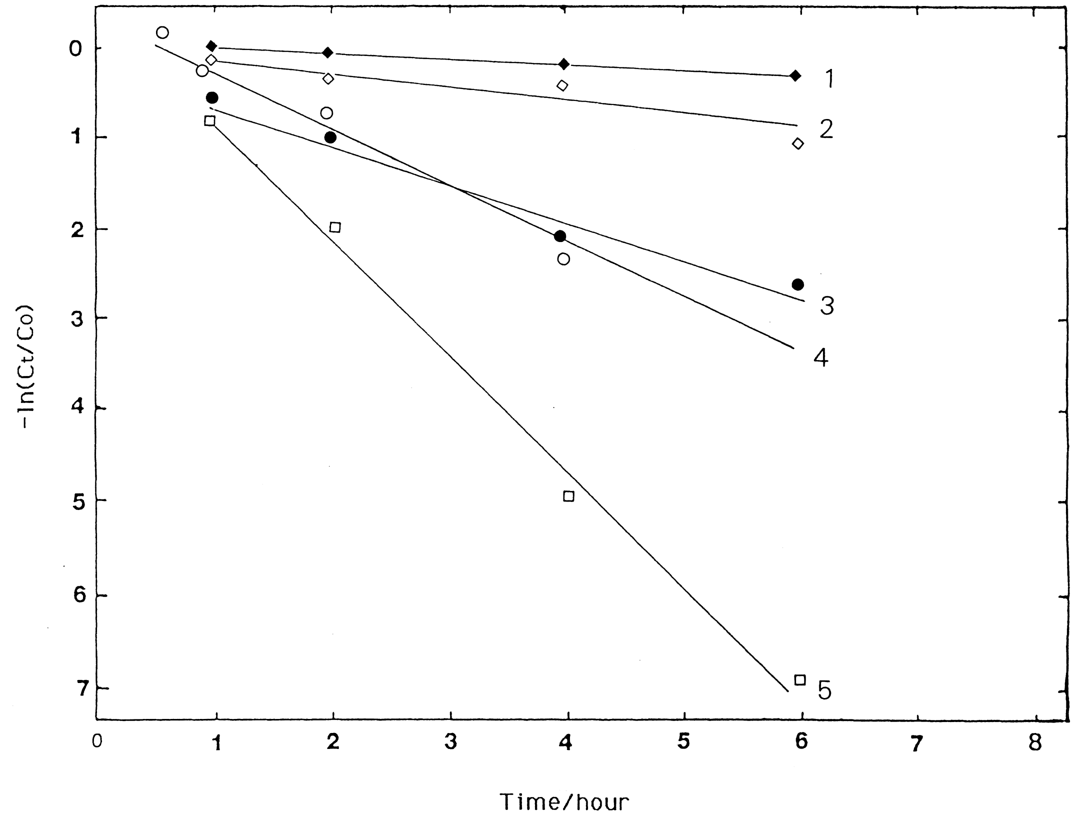

Fig. 3. First-order relations for photodegradation of fluorene in various solvents ——◆——, acetonitrile (ACCN)/water (H_2O) (50/50);——◇——, acetonitrile (ACCN)/water (H_2O) (70/30); ——○——, acetonitrile (ACCN); ——●——, methanol (MeOH); ——□——, dichloromethane (DCM).

also included in Table 1. Those in ACCN for fluorene and 1-methylfluorene are 1.48 and 1.07, respectively.

By comparing the above results, obtained on ACCN solutions, with those on DCM, effect of solvent was studied on 1-methylfluorene and 2-nitrofluorene. In both ACCN and DCM, 1-methylfluorene mostly disappeared upon 6 h of irradiation. Solid line 3 and dotted line 3′ in Fig. 5 respectively indicate kinetic relations on ACCN and DCM solutions of 1-methylfluorene. For comparison, the relation obtained on ACCN solution of fluorene is given by line 2. According to lines 2 and 3, it can be seen that the stability of 1-methylfluorene is almost equal to that of fluorene. On

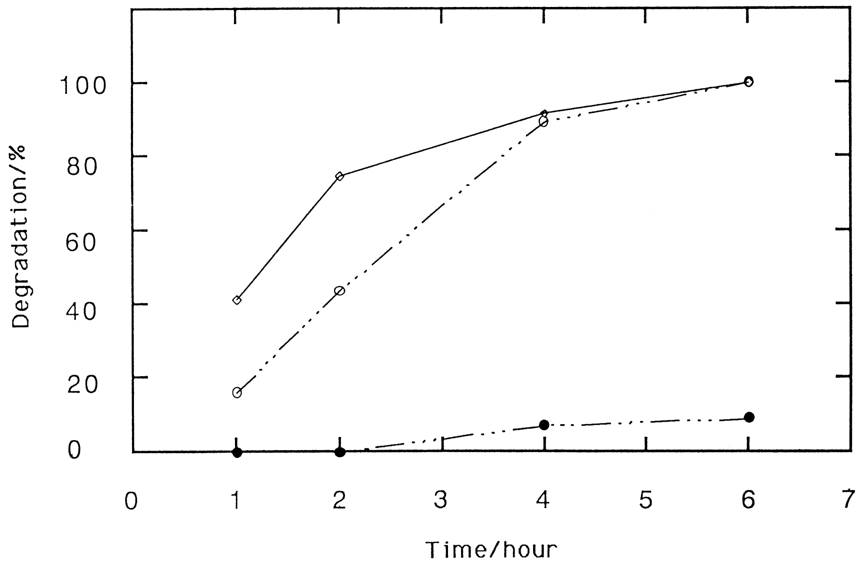

Fig. 4. Effect of substituent group on photodegradation (%) of fluorene. Solvent: acetonitrile (ACCN). ——□——, 1-methylfluorene; ——○- - -, fluorene; ——●- - -, 2-nitrofluorene.

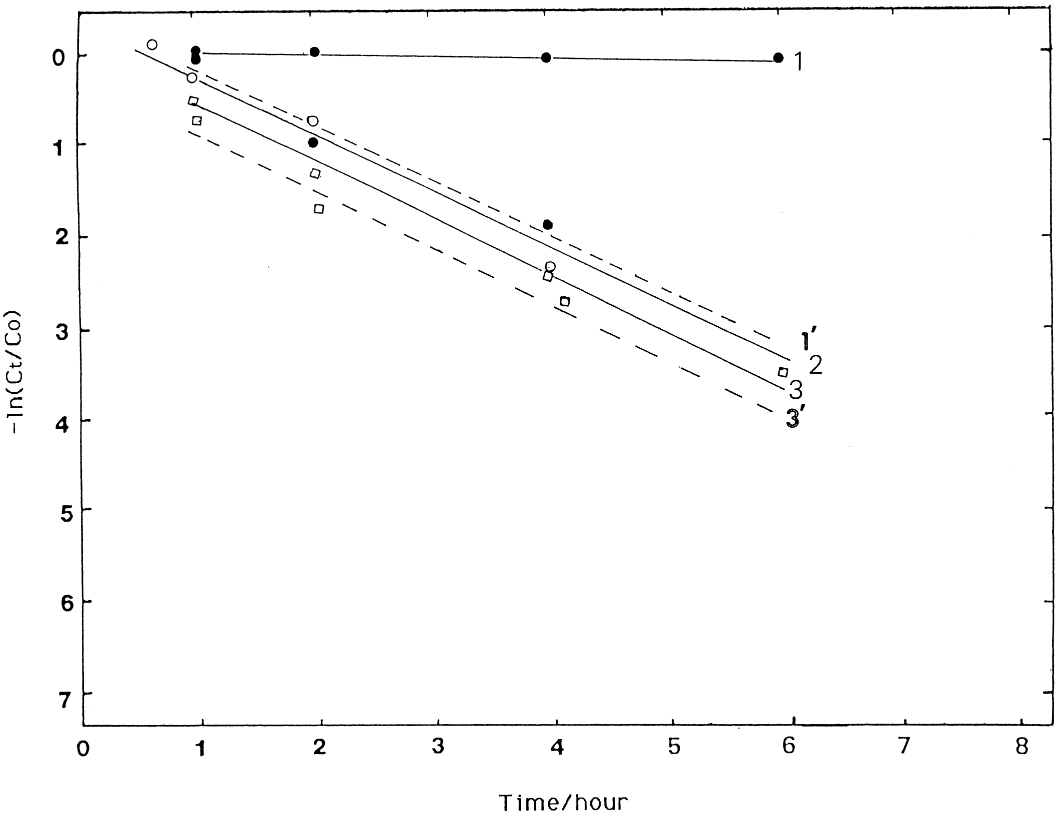

Fig. 5. First-order relations for photodegradation of fluorene and its derivatives. —●—, 2-nitrofluorene in acetonitrile (ACCN); —●- - -, 2-nitrofluorene in dichloromethane (DCM); —○—, fluorene in acetonitrile (ACCN); —□—, 1-methylfluorene in acetonitrile (ACCN); —□- - -, 1-methylfluorene in dichloromethane (DCM).

the other hand, degradation of 2-nitrofluorene in DCM upon a 2-h irradiation was 2–3%, and after 6 h of irradiation, it became 17%. As 2-nitrofluorene was degraded by 9.4% in ACCN solution in the same irradiation time, the reaction in DCM occurs faster than in ACCN. The kinetic relation for DCM solution of 2-nitrofluorene is also given by the dotted line 1′ in Fig. 5 (solid line 1 shows the relation obtained on ACCN solution.). Furthermore, both the rate constant and quantum yields are indicated in Table 1 along with the half-life. Values on DCM solution of 1-methylfluorene are close to those obtained on ACCN solution. In contrast, the rate constant and quantum yield for 2-nitrofluorene in DCM increased more than ten times compared with those in ACCN.

3.2. *Comparison of degradation products*

Fluorene (**I**) gave only one product peak on a gas chromatogram obtained under our analytical condition. The component of the peak was identified as 9-fluorenone (**II**) by a spectral database of GC/MS. An absorption spectrum obtained by a reversed phase HPLC equipped with a photodiode array detector also showed the formation of **II** as a major product. These results coincide with those reported by Cavill et al. [18], Santamaria et al. [19] and Barbas et al. [14]. An HPLC chromatogram furthermore showed the presence of another compound elution before **II**. This indicates that minor polar products which did not appear on a gas chromatogram are formed. In case of fluorene, use of a different kind of solvent had no effects on components of products. Furthermore it was confirmed that 9-fluorenone (**II**), formed by the oxidation of fluorene, is very stable under irradiation by light. 1-methylfluorene (**III**) also showed one product peak on a gas chromatogram. Despite it, identification of this major product was difficult. Candidates for the product obtained by a spectral database of GC/MS were phenanthrol, anthrone(anthracenone) and methylbenzo[c]-cinnoline. In case of **III**, occurrence of two types of oxidation reactions: oxygen attack on methyl group and that of methylene group on fluorene skeleton, are presumable. Molecular weight of the resulting product is expected to be 194. Fig. 6 shows EI mass spectrum obtained for a major product from **III**. It includes M^+ at *m*/*z* 194 and fragment ions at *m*/*z* 165, 139, 97, 82 and 69. If the methyl group is oxidized, 1-fluorenecarbaldehyde should be formed. We compared this mass spectrum with that of 2-fluorenecarbaldehyde (1-fluorenecarbaldehyde was not commercially available). Consequently, both spectra coincided with each other very well and it is supposed that the product is 1-fluorenecarbaldehyde. However, the retention time of product peaks observed on GC and HPLC chromatograms were considerably different from that of 2-fluorenecarbaldehyde.

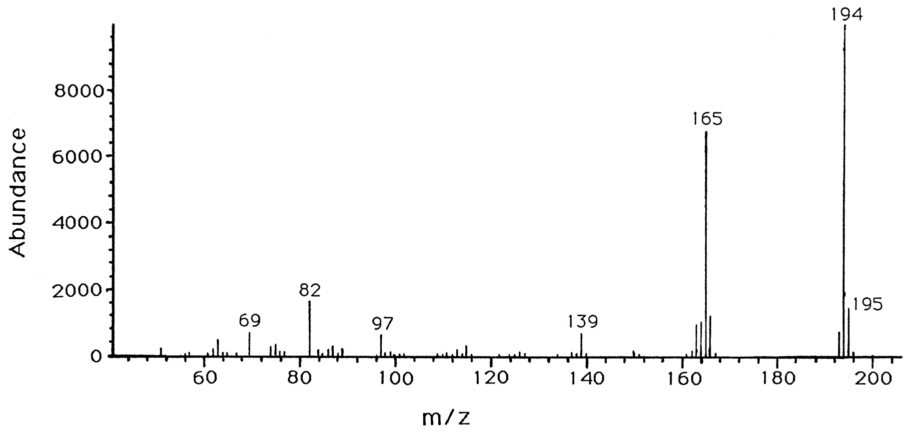

Fig. 6. EI mass spectrum of a major photodegradation product from 1-methylfluorene.

Moreover, the absorption spectrum obtained for a product peak (Fig. 7A) using a photodiode array absorbance detector in HPLC differed from that of 2-fluorenecarbaldehyde (Fig. 7B), and it was similar to that of fluorenone (Fig. 7C), maximum absorption at 260 nm). The spectrum of the product was about 1 nm red shifted as a whole. Difference in mass number between M^+ (194) and the largest fragment ion (165) is 29. Although this corresponds to CHO, the non-formation of aldehyde is indicated by the absorption spectrum measured on HPLC. Loss of CHO has been observed for not only aromatic aldehyde but also other aromatic compounds [20,21] which show simultaneous dissociation

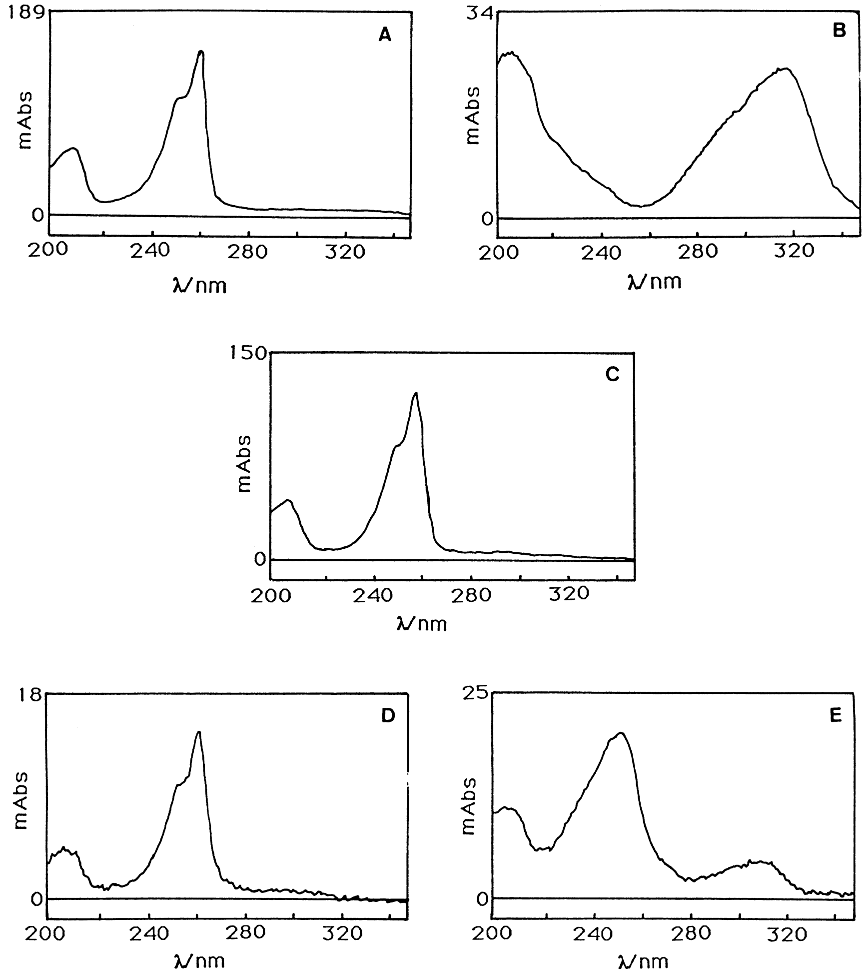

Fig. 7. Comparison of absorption spectra observed with photodiode array detector in HPLC analysis. (A) a product of 1-methylfluorene; (B) 2-fluorenecarbaldehyde; (C) fluorenone; (D) a product of 2-nitrofluorene; (E) benzo[c]cinnoline.

of hydrogen, H, with CO (e.g. 9,9′-dianthraquinone, 4,7-dimethylbenzofuran). Judging from this kind of possibility and the similarity of the absorption spectrum to that of fluorenone, we tentatively identified the major product as 1-methylfluorenone (**IV**) which has a molecular weight of 194. The presence of methyl and carbonyl group in molecular structure could not be confirmed by other techniques, since the concentration of the product was not sufficient to detect. It should be noted that 1-methylfluorenone was not commercially available. In addition to the major product, other minor products appeared on the HPLC chromatogram.

Analysis of reaction products from 2-nitrofluorene (**V**) was possible on solutions irradiated for more than 4 h. A DCM solution irradiated for 4 h, when 12.3% of **V** degraded, gave two product peaks before retention time of **V** on a gas chromatogram. The mass spectrum of the first peak, which is a minor product and had a smaller retention time, had M^+ at *m/z* 200 and fragment ions at *m/z* 165 and 82. This compound was identified as 2-chlorofluorene by a spectral database of GC/MS. The second peak, of which yield increased with irradiation time and became a major product, gave a mass spectrum with M^+ at *m/z* 214 and fragment ions at *m/z* 186, 151,125, 93 and 75, which is shown in Fig. 8. A compound which has the most similar mass spectrum to that of this product, selected by a spectral database of GC/MS, was chlorobenzo[c]cinnoline. According to GC/MS/MS data, a fragment ion *m/z* 186 is produced by releasing CO or N_2 (−28) from *m/z* 214 ion and *m/z* 151 is produced by releasing Cl (−35) from *m/z* 186 ion. On the assumption that CO is released, the product is considered to be chlorofluorenone with a molecular weight of 214. The absorption spectrum, obtained with a photodiode array absorbance detector in HPLC analysis, for a product (Fig. 7D), which corresponds to the second peak on a gas chromatogram, supports this assumption that the product has a ketone structure. The spectrum was quite different from that of non-substituted benzo[c]cinnoline (Fig. 7E) and had a characteristic feature of fluorenone (Fig. 7C). The absorption maximum was about 3 nm red shifted compared with fluorenone. Thus, the product with M^+ at 214 was tentatively identified as 2-chlorofluorenone (**VI**). Hence, a major reaction for degradation of 2-nitrofluorene involves a replacement reaction by chlorine atom derived from DCM (trace contaminants including chlorine atoms also behave similarly as described below). Furthermore, HPLC and GC/MS/MS data implied that a 4-h irradiated solution contains trace amount of a polar compound with M^+ at 225, which is considered to be 2-nitrofluorenone (**VII**). By irradiating for 6 h, degradation in DCM increased up to 17% and the yields of all products increased. It should be noted that irradiated ACCN solution also contained lesser amounts of the same products with M^+ at *m/z* 200 and 214. This may be due to the presence of chlorine source as trace contaminants probably in glasswares or in reagents used for experiments.

The photostability of other substituted fluorenes: 9-fluorenecarboxylic acid (**VIII**) and 9-fluoreneacetic acid (**IX**), was compared with that of fluorene. ACCN solutions of both compounds were irradiated under the same conditions. Photodegradation products were analyzed using GC/MS and reversed phase HPLC. Results showed that both compounds are unstable under light. However, it was impossible to obtain kinetic data using the chromatographic area obtained by GC/MS, since these substrates decompose by heat in GC/MS analysis. The products from 9-fluorenecarboxylic acid contained fluorene (**I**) (this compound overlapped with **VIII** in GC/MS, but is separately detected by HPLC) and 9-fluorenone (**II**). 9-Fluorenone (**II**) is the main product of photodegradation for **VIII**. An increase in the yield of this compound was observed, by both GC/MS and HPLC (thermal decomposition can be eliminated), with increasing irradiation time. **II** may be formed by oxidation of a primary product, fluorene. One more substituted fluorene 9-fluoreneacetic acid (**IX**) was also converted to **I** and **II**. The mechanism for the formation of **II** is probably the same as the case of **VIII**.

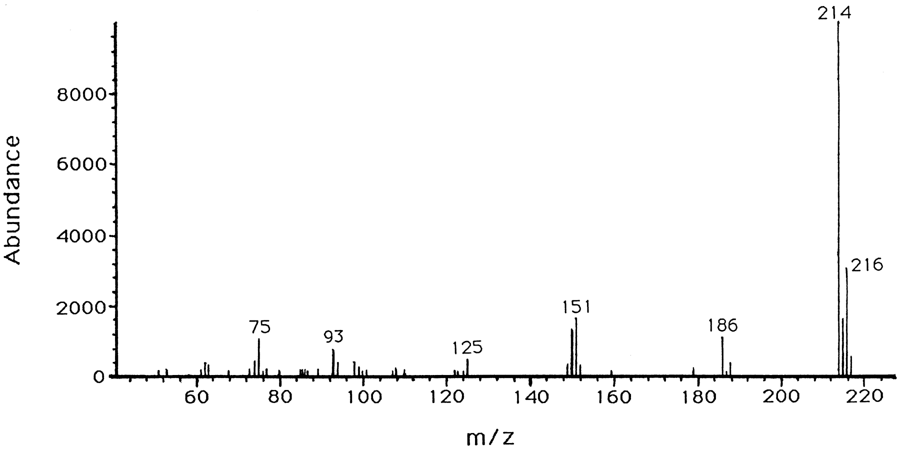

Fig. 8. EI mass spectrum of a major photodegradation product from 2-nitrofluorene.

4. Discussion

The effect of solvent on photodegradation of fluorene and its derivatives is apparent from the results. Degradation (%) and quantum yield decreased in the order of DCM > ACCN > MeOH > ACCN/H_2O (70/30) > ACCN/H_2O(50/50). This order may be strongly related to the solubility of oxygen in a solvent. In general, the solubility of gas (in this case, oxygen) increases as the solvent polarity decreases [22]. According to this general rule and measured values [22,23], the content of oxygen for DCM is the largest and decreases in the order of ACCN, MeOH and water. Good correlation is obtained between our results for degradation and the solubility of oxygen obtained from the solvent polarity. Concerning mixtures of ACCN and water, we had two pieces of evidence which explain why the rate of oxidation reaction decreases. The evidence implies the occurrence of a decrease in the solubility of oxygen by adding water to ACCN. One piece of the evidence is the observation of a decrease in fluorescence quenching by oxygen. For example, the fluorescence intensity of fluorene increased with increasing the water content in a mixture and finally approached the strongest level measurable on deoxygenated solution. This indirectly means that the solubility of oxygen decreases with increasing water content. Further evidence was obtained by the measurement of solvated oxygen peaks which appeared in reversed phase HPLC [24]. Solvated oxygen shows weak absorption below 240 nm and this can be applied to detection of oxygen in a mixture of ACCN/H_2O. Fig. 9 shows changes in the intensity of solvated oxygen peak (with asterisk, $R_t = 4.75$ min) with varying the water content. The results indicate that the oxygen content decreases with increasing the water content. Low reactivity observed on two ACCN/H_2O solutions can be partly explained by these facts. Cluster structure of ACCN/H_2O system [25] may affect the solubility of oxygen. In addition to the solubility of oxygen, the reactivity of fluorene and 1-methylfluorene may be affected by the polarity of solvent itself, the viscosity and solvation effect for the solvent. In case of 2-nitrofluorene, degradation by oxidation reaction seems to be depressed by the presence of nitro-group (this has electron withdrawing character) at the 2-position of the fluorene skeleton.

Some PAHs such as anthracene, phenanthrene and tetracene are good acceptors of singlet oxygen ($^1O_2$) [14]. However, it has been reported that reaction of fluorene with $^1O_2$ proceeds very slowly [26]. Therefore, Barbas et al. [14] supposed that direct photolysis of fluorene to give fluorenone at a silica gel/air interface is not mediated by $^1O_2$. Instead, they proposed an electron transfer mechanism for the formation of fluorenone. This time, using a singlet oxygen trap, 2,5-dimethylfuran, we re-examined whether fluorene and its derivatives reacted with $^1O_2$ or not. If the kind or the distribution of reaction products changes when singlet oxygen trap is added, $^1O_2$ is concerned with the oxidation reaction. Our results (5-h irradiation) showed no change in the kind and distribution of products. Hence, we can conclude that the degradation of fluorene and its derivatives is not mediated by $^1O_2$. Therefore, we also suppose, as Barbas et al. [14] did, that oxidation of fluorene and its derivatives occurs by another mechanism. Judging from reaction products, the electron transfer mechanism is the most acceptable. However, a proof for the formation of ground state complex between substrate and oxygen was not observed in the UV-VIS absorption spectrum. Probably, contact charge transfer pairs between substrate and molecular oxygen are present in solution and they may, by excitation, form a complex and generate radical species which react with molecular oxygen.

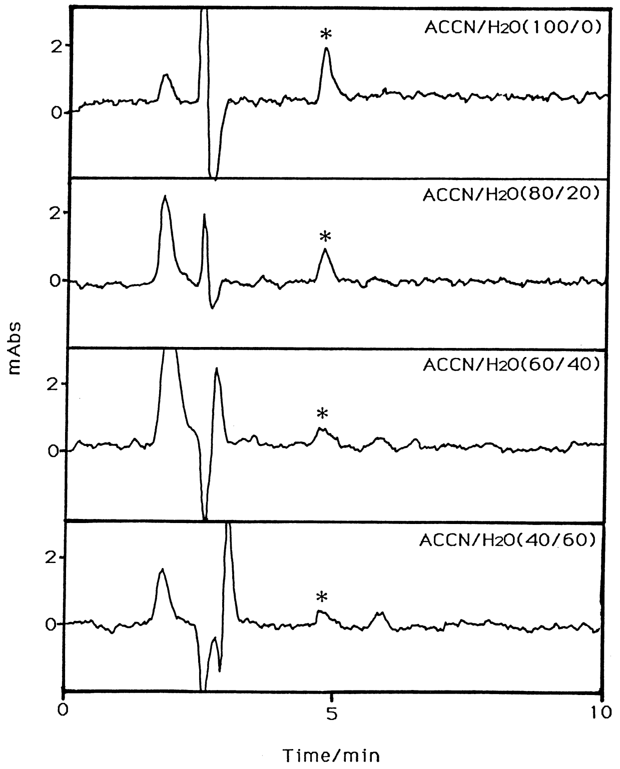

Fig. 9. Change in the intensity of solvated oxygen peak in HPLC with varying water content in acetonitrile. Solvated oxygen peak is marked by an asterisk. Chromatograms were obtained by observing the absorbance at 210 nm.

The effect of the substituent group on photodegradation was large in case of 2-nitrofluorene. Good photostability was observed for this compound. In addition, it was shown that the presence of chlorine source (as a solvent or a contaminant) induces a replacement reaction, which results in the formation of 2-chlorofluorene. It seems that the primary product 2-chlorofluorene is further oxidized and transformed to 2-chlorofluorenone. According to our results, the probability of direct oxidation forming 2-nitrofluorenone seems very small. Effect of alkyl group on the stability of PAH has been previously reported by some researchers. Munoz et al. [27] reported that alkylation of PAH decreases the stability for biodegradation. On the contrary, Kennicutt

[28] and Anderson [29] presented opposite results. Kennicutt reported that alkylation of phenanthrene increases the stability for biodegradation. A similar tendency was observed by Anderson [29] in case of photodegradation. We think it is very difficult to discuss the photostability from only the presence or absence of a substituent group. The reactivity differs depending on the position of the substituent group on an aromatic ring system [27,29]. For example, one of the nitrated PAHs, 6-nitrobenzo[a]pyrene, shows very bad photostability [30]. This means that the nitro group does not always increase the photostability of PAH and the position of the substituent group is very important.

For photooxidation of methylated PAHs, we have speculated that oxidation occurs on the methyl group such as in the cases of methylnaphthalene [31] and methylphenanthrenes [32], However, our result on 1-methylfluorene showed that this is not common to all PAHs and oxidation of methylene carbon predominantly occurs in case of fluorene. The presence of –COOH or $-CH_2COOH$ group at the 9 position of fluorene skeleton seems not to depress the photooxidation and rather decreases the photostability (in addition to thermal stability). It seems that these substituent groups are readily lost and fluorene is formed as a primary product. Fluorene is further oxidized to 9-fluorenone according to the mechanism mentioned above.

5. Conclusions

The effect of solvent and substituent group on photooxidation of fluorene was investigated. The results showed that photooxidation rate changes depending on the solvent. The rate constant obtained for fluorene decreased in the order of DCM > ACCN > MeOH > $ACCN/H_2O/(70/30)$ > $ACCN/H_2O$ (50/50), i.e., nonpolar solvents generally gave higher values than the polar ones. This is mainly due to difference in the solubility of oxygen. 1-Methylfluorene exhibits comparable reactivity to that of fluorene. On the other hand, 2-nitrofluorene showed good photostability. However, this compound reacts in the presence of a chlorine source. Moreover, the presence of –COOH and $-CH_2COOH$ at the 9 position seemed to decrease both photochemical and thermal stability.

References

[1] N.T. Edward, J. Environ. Qual. 12 (1983) 427–441.
[2] T. Nielsen, T. Ramdahl, A. Bjørseth, Environ. Health Perspect. 47 (1983) 103–114.
[3] J.N. Pitts, Environ. Health Perspect. 47 (1983) 115–140.
[4] H. Pyysalo, J. Tuominen, K. Wickström, E. Skyttä, L. Tikkanen, S. Salomaa, M. Sorsa, T. Nurmele, T. Mattila, V. Pohjola, Atmospheric Environ. 21 (1987) 1167–1180.
[5] D. Helmig, J. Arey, R. Atkinson, W.P. Harger, P.A. McElroy, Atmospheric Environ. 26 (1992) 1735–1745.
[6] M.P. Ligocki, C. Leuenberger, J.F. Pankow, Atmospheric Environ. 19 (1985) 1609–1617.
[7] R.M. Dickhut, K.E. Gustafson, Environ. Sci. Technol. 29 (1995) 1518–1525.
[8] K. Pointet, M.-F. Renou-Gonnord, A. Milliet, P. Jaudon, Bull. Soc. Chim. Fr. 134 (1997) 133–140.
[9] W.F. Rogge, L.M. Hildemann, M.A. Mazurek, G.R. Cass, Environ. Sci. Technol. 27 (1993) 636–651.
[10] D. Golomb, D. Ryan, J. Underhill, T. Wade, S. Zemba, Atmospheric Environ. 31 (1997) 1361–1368.
[11] J.A. Lebo, L.M. Smith, J. Assoc. Off. Anal. Chem. 69 (1986) 944–951.
[12] D.M. Wagrowski, R.A. Hites, Environ. Sci. Technol. 31 (1997) 279–282.
[13] T.D. Behymer, R.A. Hits, Environ. Sci. Technol. 19 (1985) 1004–1006.
[14] J.T. Barbas, M.E. Sigman, R. Arce, R. Dabestani, J. Photochem. Photobiol. A: Chem. 109 (1997) 229–236.
[15] T. Mill, W.R. Mabey, B.Y. Lan, A. Baraze, Chemosphere 10 (1981) 1281–1290.
[16] R.G. Zepp, Environ. Sci. Technol. 12 (1978) 327–329.
[17] W.M. Draper, Chemosphere 14 (1985) 1195–1203.
[18] G.W.K. Cavill, A. Roberson, W.B. Whalley, J. Chem. Soc. (1949) 1567–1570.
[19] J. Santamaria, R. Jroundi, Tetrahedron Lett. 32 (1991) 4291.
[20] J.H. Beynon, R.A. Saunders, A.E. Williams, The Mass Spectra of Organic Molecules, Elsevier, Amsterdam, 1968.
[21] H. Budzikiewicz, C. Djerassi, D.H. Williams, Mass Spectrometry of Organic Compounds, Holden-Day, San Francisco, CA, 1967.
[22] S.R. Bakalyar, M.P.T. Bradley, R. Honganen, J. Chromatogr. 158 (1978) 277–293.
[23] E. Heftmann, Chromatography, Van Nostrand Reinhold, New York, 1975.
[24] Jo Doehl, J. Chromatogr. Sci. 26 (1988) 7–11.
[25] A. Wakisaka, Y. Shimizu, N. Nishi, K. Tokumaru, S.J. Sakuragi, J. Chem. Soc., Faraday Trans. 88 (1992) 1129–1135.
[26] W. Mabey, J.H. Smith, R.T. Podoll, H.L. Johnson, T. Mill, T.W. Chou, J. Gate, I. Waight-Partridge, H. Jaber, D. Vandenberg, Rep. EPA-440/4-81-14, US Environmental Protection Agency, 1982.
[27] D. Munoz, P. Doumenq, M.C. Elhy, M. Guilano, F. Jacquot, P. Scherrer, G. Mille, Polycyclic Aromatic Compounds 9 (1996) 129–136.
[28] M.C. Kennicutt, Oil Chem. Pollut. 4 (1988) 89–112.
[29] J.T. Anderson, Chemosphere 27 (1993) 2097–2102.
[30] R.M. Kamens, F. Zhi-Hua, Y. Yao, D. Chen, S. Chen, M. Vartiainen, Chemosphere 28 (1994) 1623–1632.
[31] J.T. Barbas, M.E. Sigman, A.C. Buchanan III, E.A. Chvis, J. Photochem. Photobiol. A: Chem. 58 (1993) 155–158.
[32] S. Matsuzawa, L. Moeini-Nombel, Polycyclic Aromatic Compounds, Gordon and Breach, London, in press.