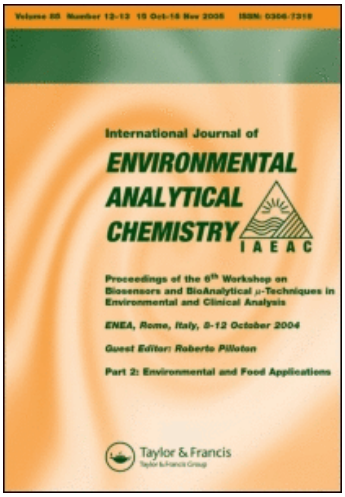



International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Photooxidation of Selected Polycyclic Aromatic Hydrocarbons in Aqueous Organic Media in The Presence of Ti(IV)Oxide

K. C. Swallow[ab]; K. Taghizadeh[a]; S. Weakland[a]; E. F. Plummer[a]; W. F. Busby Jr[a]; A. L. Lafleur[a]
[a] Center for Environmental Health Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA [b] Department of Chemistry, Merrimack College, North Andover, MA, USA

**To cite this Article** Swallow, K. C. , Taghizadeh, K. , Weakland, S. , Plummer, E. F. , Busby Jr, W. F. and Lafleur, A. L.(1995) 'Photooxidation of Selected Polycyclic Aromatic Hydrocarbons in Aqueous Organic Media in The Presence of Ti(IV)Oxide', International Journal of Environmental Analytical Chemistry, 60: 2, 113 — 122
**To link to this Article: DOI:** 10.1080/03067319508042869
**URL:** http://dx.doi.org/10.1080/03067319508042869

*Intern. J. Environ. Anal. Chem.*, Vol. 60, pp. 113–122
Reprints available directly from the publisher
Photocopying permitted by license only



# PHOTOOXIDATION OF SELECTED POLYCYCLIC AROMATIC HYDROCARBONS IN AQUEOUS ORGANIC MEDIA IN THE PRESENCE OF Ti(IV)OXIDE

*K. C. SWALLOW, K. TAGHIZADEH, S. WEAKLAND, E. F. PLUMMER, W. F. BUSBY, JR. and A. L. LAFLEUR

*Center for Environmental Health Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA*

*(Received, 16 August 1994; in final form, 17 October 1994)*



We have studied the photooxidation of selected polycyclic aromatic hydrocarbons (PAH) in the presence of Ti(IV)oxide in a mixed solvent system consisting of N-methylpyrrolidinone (NMP) and water. Reaction rates for the photooxidation of acenaphthylene and pyrene were investigated by monitoring the disappearance of the PAH substrate from the reaction mixture as a function of time. For both compounds plots of $\ln C_o/C_t$ as a function of time yielded straight lines, indicating first order kinetics with respect to the substrate. With an initial acenaphthylene concentration of 1.0 $gL^{-1}$ the first order reaction rate constant was 0.19 $hr^{-1}$ and the half life was 3.7 hr. With an initial pyrene concentration of 0.2 $gL^{-1}$ the first order reaction rate constant was 0.0285 $hr^{-1}$ and the half life was 24 hr. The photoproducts were characterized by high performance liquid chromatography with diode-array detection (HPLC/DAD) and by liquid chromatography/atmospheric pressure chemical ionization mass spectrometry (APCI/LC-MS). Although a number of simple oxidation products were identified the bulk of the photoproducts consisted of the parent PAH substituted with one or more solvent (NMP) molecules. The product mixtures from the photooxidation of the non-mutagens acenaphthylene and pyrene were found to be also non-mutagenic in our *Salmonella typhimurium* forward mutation assay.

**KEY WORDS:** Photooxidation, polycyclic aromatic hydrocarbons (PAH), titanium dioxide, acenaphthylene, pyrene, cyclopenta[*cd*]pyrene.

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are produced during combustion as a direct consequence of imperfect mixing of fuel and air, a situation often encountered in common combustors such as power plants, domestic furnaces and automobiles[1]. Thus, PAH have become ubiquitous environmental pollutants in air, soil and water[2,3]. Some PAH are mutagenic or tumorigenic in *in vivo* and *in vitro* assays and their presence in the environment can pose a risk to human health[1–7]. The relative abundances of PAH found in sediments are similar to those found at the combustion sources[8], suggesting that PAH are stable in the environment. However, evidence suggests that other combustion-generated PAH may be rapidly degraded in the atmosphere by photooxidation. In particular, it has been suggested[9] that cyclopenta-fused PAH, which are markedly

* To whom correspondence should be directed.
Department of Chemistry, Merrimack College, North Andover, MA 01845, USA

abundant in combustion emissions[1,6], are scarce in atmospheric particulates because of their susceptibility to photooxidation.

In order to learn more about the susceptibility of different types of PAH to photooxidation, we have studied the photooxidation of three PAH; acenaphthylene (Acl), pyrene (Pyr), and cyclopenta[*cd*] pyrene (CPP) in the presence of Ti(IV)oxide in a binary solvent solution consisting of nine parts N-methylpyrrolidinone (NMP) to one part water. This solvent system was chosen to provide the surface and moisture conditions thought to be essential for simulating particulate phase photooxidation in airborne particulates while permitting the use of solutions of sufficient volume and concentration to test for mutagenicity of the reaction products and to elucidate their molecular structures. The use of NMP also permits the technique to be explored as a practical method for the large-scale destruction of PAH-containing hazardous waste. The three PAH were selected for this study because acenaphthylene is the most abundant vapor-phase PAH and cyclopenta[*cd*]pyrene is the most abundant soot-bound PAH formed in hydrocarbon flames[1,6] and pyrene is nearly ubiquitous in the environment[2].

In general, photooxidation rates are determined experimentally either by monitoring the disappearance of substrate[8] or the evolution of $CO_2$[10,11]. Some organic compounds undergo complete mineralization to $CO_2$ via photooxidation[12–14]; however, PAH can be more difficult to oxidize and experiments have shown that they can produce stable intermediate products of partial oxidation[15,16]. Thus, the possibility exists that a PAH may be partially photooxidized to a daughter compound which is actually more harmful than the original PAH. One of the aims of this study is to shed some light on the problem of whether a non-mutagenic PAH could be oxidized to a mutagenic daughter compound.



## EXPERIMENTAL

### *Procedure*

Solutions of three PAH; acenaphthylene (1.0 mg/mL), cyclopenta[*cd*]pyrene (0.04 mg/mL), and pyrene (0.20 mg/mL) were prepared from reagent grade solids dissolved in a mixed solvent of 90% NMP and 10% $H_2O$. The mixed solvent system served the dual purpose of completely dissolving both the starting PAH and the reaction products from the photooxidation and providing water from which hydroxyl radicals are produced at the surface of the titanium dioxide. A weighed portion of Ti(IV)oxide, 99.9+% anatase (Aldrich Chemical Co.) was added to each solution. The average particle size of the anatase powder was 0.4 μm.

Photolysis of the solutions was carried out either in a 250 mL borosilicate photochemical reaction vessel (Ace Glass: Vineland, NJ; no. 7863–16) or in a borosilicate sample tube mounted in a photochemical turntable reactor (Ace Glass: no. 7891). In the first case a magnetic stirring bar was placed in the reaction vessel and a 100 W, medium pressure, quartz Hg arc lamp (Ace Glass: 7825–30) in a water-cooled borosilicate immersion well (Ace Glass 7875B-35) was placed in the center of the vessel and held in place with a fluorocarbon-sealed compression collar. In the second case the filled tubes were sonicated for 15–30 minutes to suspend the Ti(IV)oxide. The suspensions were stable over the course of the experiments. The filled tubes were placed in the turntable which rotated around the water cooled borosilicate immersion well containing the quartz Hg arc lamp. The apparatus was placed inside a Photochemical Safety Reaction Cabinet (Ace Glass: no. 7836) and a sample was withdrawn at time zero.

The lamp was turned on and subsequent samples were withdrawn at periodic intervals up to 96 hours.

*Chemical analysis*

After filtering each sample with a 0.2 μm fluorocarbon filter to remove the Ti(IV) oxide, the PAH substrate concentration was determined by high performance liquid chromatography (HPLC). The HPLC instrument used for monitoring PAH substrate disappearance and product formation consisted of a Hewlett-Packard model 1082B binary pumping system with variable wavelength detector set at 280 nm. The column was 250 mm in length and 10 mm in diameter. It was packed with Jordi-Gel 500 poly(divinylbenzene) (PDVB) material having a particle diameter of 5 μm. The mobile phase was N-methylpyrrolidinone maintained at 50°C. The flow rate was 1.0 mL/min.

With this column and mobile phase combination, retention is governed by a multimodal mechanism combining steric exclusion with reverse phase processes[17]. It permits the separation of PAH starting materials from their more polar photoproducts, (polar species elute earlier), and facilitates the collection of products for further HPLC analysis. Using similar mobile phase and photoreaction media reduces sample preparation to one filtration step and facilitates further analysis by reverse-phase HPLC.

Samples were also analyzed by HPLC with spectrophotometric diode-array detection (HPLC/DAD) and by liquid chromatography with atmospheric pressure chemical ionization mass spectrometry (APCI/LC-MS). The HPLC/DAD instrument was a model 1090 liquid chromatograph obtained from Hewlett-Packard. The diode-array detector provided the absorption spectrum of each component over the range 220 to 500 nm. The APCI/LC-MS instrument was a Perkin-Elmer/Sciex API-I model equipped with a ternary pumping system and diode-array detector from Beckman Instruments. For analytical separations, we used a Vydac 201TP54 C18 reverse phase column (Separations Group, Hesperia, CA) with gradient elution from 95% $H_2O$:5% acetonitrile to 100% acetonitrile over 40 minutes.

Some samples were also analyzed by gas chromatography-mass spectrometry. The instrument consisted of a Hewlett-Packard Model 5890/II Gas Chromatograph with a DB-5 fused silica capillary column of length 30 m, film thickness 0.1 μm, and diameter 0.25 mm, and a Model 5971 Mass Selective Detector operating in electron-impact mode at an ionizing energy of 70 eV. The injector and detector were maintained at 320°C. The column temperature was ramped linearly from 100 to 320°C at 10°C/min., and then held at 320°C for 10 minutes.

*Mutation assay*

The mutagenic activity of the samples was determined in *Salmonella Typhimurium* utilizing 8-azaguanine resistance as the genetic end point[18,19]. Frozen aliquots of strain TM677 were grown in minimal media supplemented with 2% brain heart infusion and treated for 2 hr at 37°C in a liquid suspension with the samples at total concentrations of 0–300 g/mL. This was done both in the presence or absence of a 5% (v/v) Aroclor-1254 induced rat liver postmitochondrial supernatant (PMS). Cultures treated with PMS contained an NADPH generating system. Stock solutions of extracts were prepared in dimethyl sulfoxide (DMSO). A 10 uL aliquot of stock solution was added to 0.99 mL of bacteria with or without PMS and the NADPH generating system.

Bacteria were plated in triplicate on minimal agar plates in the presence or absence of 50 g/mL of 8-azaguanine (8AG), incubated at 37°C and counted 2 days later. The number of mutant colonies observed divided by the plating efficiency of the culture multiplied by the dilution factor yields an estimate of the mutant fraction (MF). The operational definition of a bacterial mutagen in this type of assay is a sample which induces a response greater than the 99% upper confidence limit for the background. The dose of mutagen yielding a mutant fraction equal to the 99% upper confidence limit is referred to as the minimum detectable mutagen concentration or MDMC. A positive and negative control is also tested in the same way for every sample.

## RESULTS AND DISCUSSION

### *Reaction kinetics*

The reaction rates for the photooxidation of acenaphthylene and pyrene were investigated by monitoring the disappearance of the PAH substrate from the reaction mixture as a function of time. Figure 1 shows the plot for acenaphthylene and Figure 2 shows that of pyrene. For both compounds plots of $\ln [C_o/C_t]$ as a function of time yielded straight lines, indicating first order kinetics with respect to the substrate. With an initial acenaphthylene concentration of 1.0 $gL^{-1}$ the first order reaction rate constant was 0.187 $hr^{-1}$ and the half life was 3.7 hr. A correlation coefficient ($R^2$) of 0.992 indicated a highly linear fit for the data.



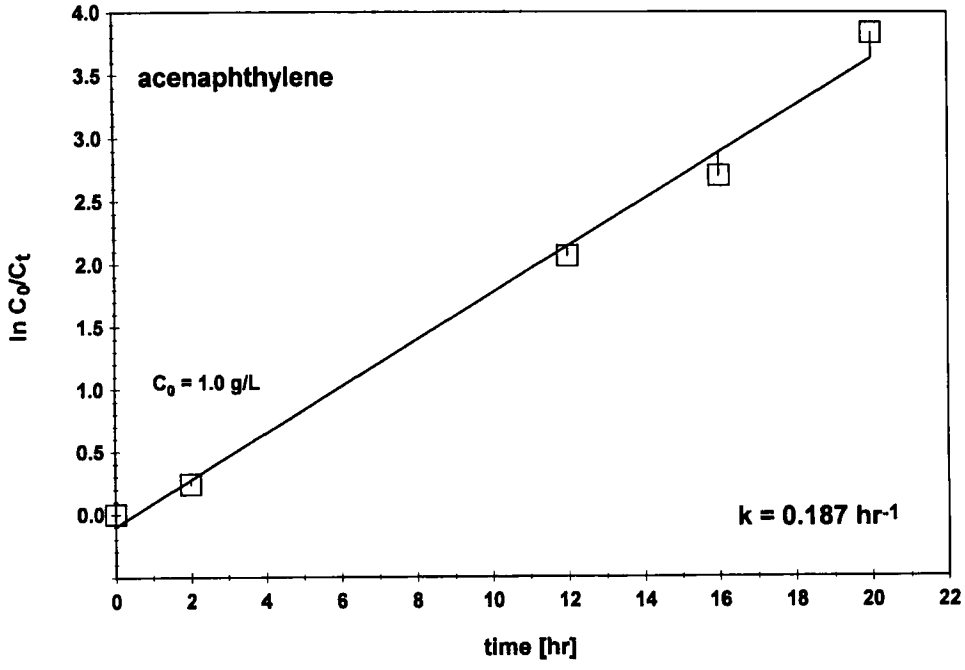



**Figure 1** First order integrated rate law plot for acenaphthylene.

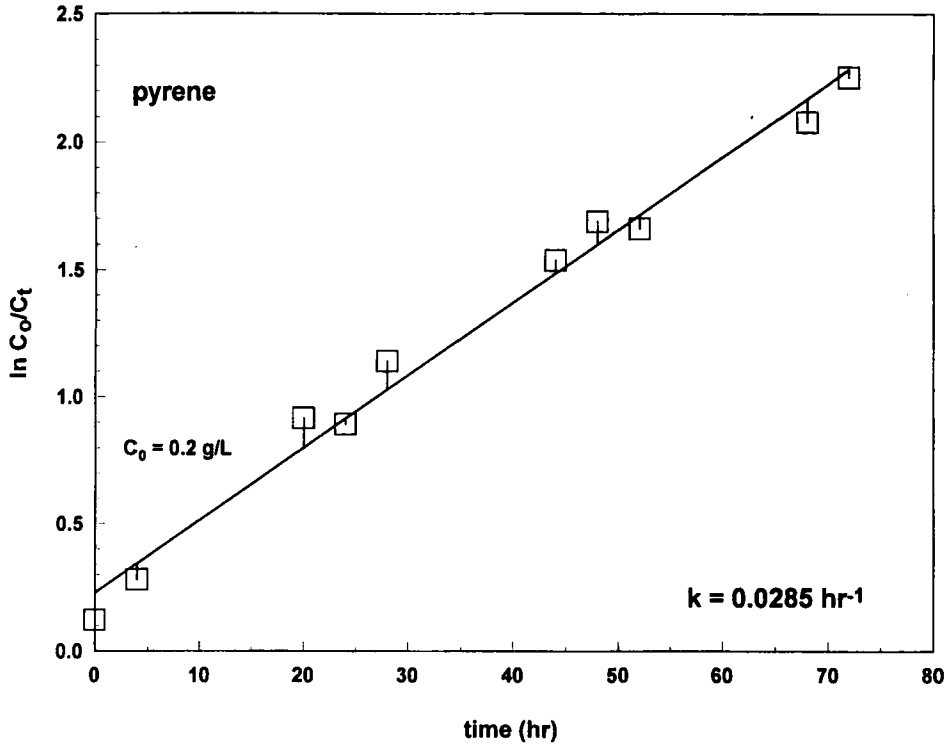



**Figure 2** First order integrated rate law plot for pyrene.



With an initial pyrene concentration of 0.2 $gL^{-1}$ the first order reaction rate constant was 0.0285 $hr^{-1}$ and the half life was 24 hr. The correlation coefficient ($R^2$ = 0.986) also indicated a highly linear fit. These half life values are in good agreement with values reported by Behymer and Hites[8] for photooxidation of acenaphthylene and pyrene adsorbed on silica gel (Acl, 0.6 hr.; Pyr, 35.5 hr.) and on alumina (Acl, 1.5 hr; Pyr, 22.5 hr.).

No quantitative results could be obtained for cyclopenta[*cd*]pyrene because of its ease of oxidation in the apparatus used in this study. The same protocol used for Acl was attempted for CPP. At an initial concentration of 0.04 mg/mL, CPP vanished to trace levels between the first (2 hr) and second (10 hr) measurement intervals. CPP's high cost and potent mutagenic activity[6] militated for a new exposure protocol using a microscale apparatus. However, in spite of the lack of quantitative photooxidation data, enough photoproduct was obtained for chemical characterization.

A typical chromatogram of the photooxidation products of acenaphthylene, obtained using HPLC with a PDVB column and NMP as the mobile phase, is shown in Figure 3. Acenaphthylene and two simple oxidation products, 1,8-naphthalene dicarboxaldehyde and 1-acenaphthenol, were added to the sample to illustrate the retention behavior of the column. A chromatogram of pyrene and it photooxidation products is shown in Figure 4. The photoproducts **A**, **B** and **C**, elute in order of decreasing polarity. The identity of some photoproducts is discussed later.

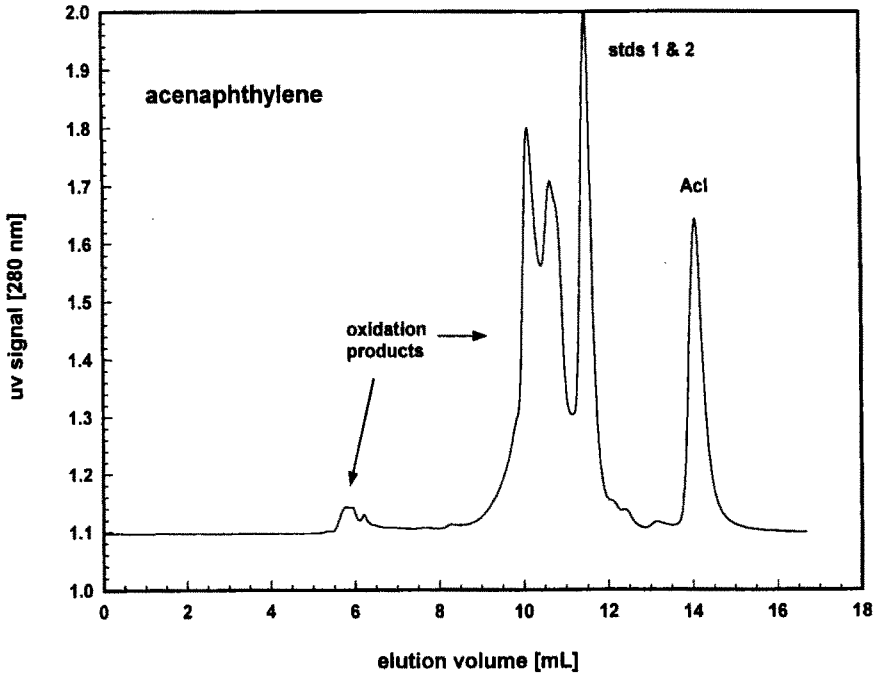



**Figure 3** Chromatogram of the oxidation products of acenaphthylene.

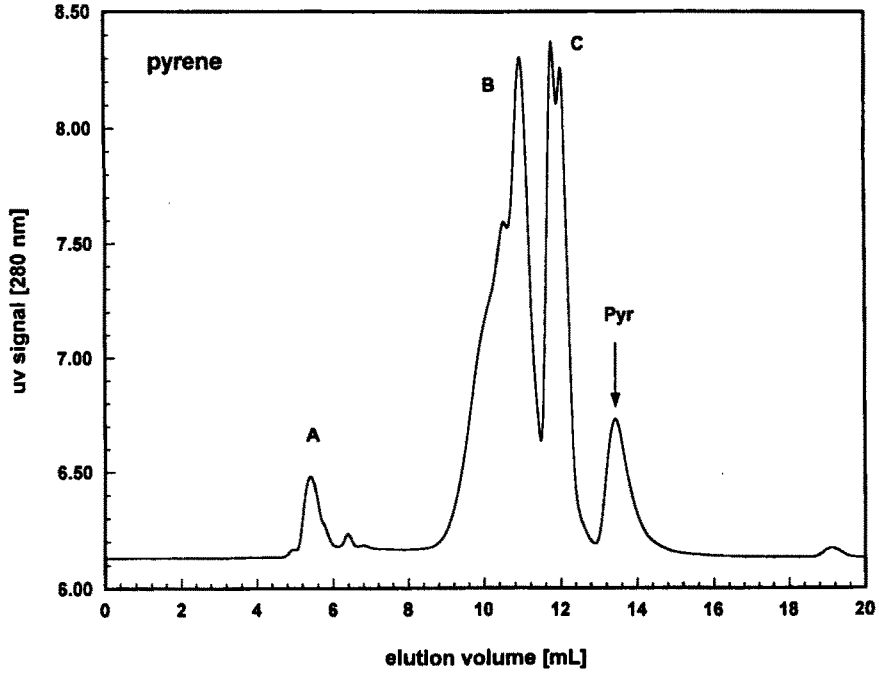



**Figure 4** Chromatogram of the oxidation products of pyrene.

*Reaction products*

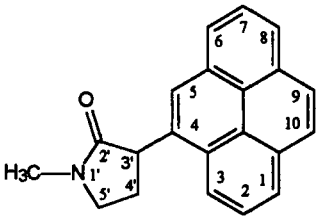
Studies on the photooxidation of benzene in the presence of aqueous titanium dioxide[20] suggest that the initial reaction occurs either directly between benzene and a photochemically generated hole on the Ti(IV)oxide surface or between benzene and a hydroxyl radical generated by oxidation of water on the Ti(IV)oxide surface. In either case, a hydroxycyclohexadienyl radical becomes the primary intermediate which further degrades via addition of a second hydroxyl group and ring cleavage to a mucondialdehyde. Further oxidation produces muconic acid and eventually carbon dioxide. This mechanism may be extrapolated to predict reaction products for fused ring compounds. Recently, the Ti(IV) oxide-catalyzed photooxidation behavior of many other types of aromatic compounds[14,21] including PAH[22] have been studied. Based on results from earlier studies[12,14,20,22], done in the presence of aqueous Ti(IV) oxide, we expected to find a number of oxygenated derivatives of Acl, Pyr and CPP as photoproducts in this study. However, the possible effect of NMP as cosolvent could not be discerned.

*Acenaphthylene*

The ultimate composition of our solvent system was determined from results of photooxidation experiments with Acl. Early work with aqueous suspensions of Acl in our apparatus showed that this system would be inadequate for the production of the milligram amounts of photoproducts necessary for mutagenicity determination in our *Salmonella typhimurium* forward mutation assay. Solvent blends such as acetonitrile/water also gave poor results. The effect of adding water-miscible solvents known for their high solvent power for PAH was tried next. Our experience with dimethyl sulfoxide (DMSO) and N-methylpyrrolidinone (NMP) made these two solvents likely candidates. Photooxidation of Acl with DMSO/water mixtures gave some expected photoproducts (e.g. **5**, **6**, and **8** in Figure 5); however, the kinetics proved to be unusual and irreproducible. The problem was traced to the production of photodimers of acenaphthylene. The production of *cis* and *trans* photodimers (cyclobuta[1,2-a: 3,4-a]diacenaphthylene)of acenaphthylene in organic media has been well studied[23-25]. Although the photodimerization reaction is reversible, with the aqueous solvent systems we were investigating the solubility of the Acl photodimer was much less than that of Acl itself and it precipitated onto the $TiO_2$ and the glass surfaces of the apparatus. Subsequent experiments with NMP led to a solution of this problem and resulted in the selection of the 9:1 NMP/water solvent system used in the work reported here. Acenaphthylene reaction mixtures obtained over a range of conditions contained variable amounts of acenaphthene quinone (**5**), naphthalene-1,8-dicarboxylic anhydride (**6**), acenaphthene (**7**), 1-acenaphthenol (**8**), naphthalene-1,8-carboxaldehyde, and naphthalene-1,8-carboxylic acid.

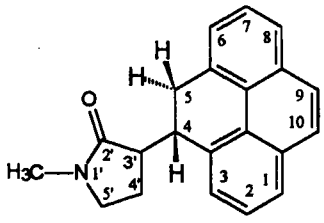
*Pyrene*

Initial chemical analysis data indicated that the pyrene reaction mixture contained small amounts of dihydroxypyrene, phenanthrene and cyclopenta[*def*]phenanthrene. The major components of the reaction mixtures, however, proved not to be the expected products of photooxidation. GC-MS and LC-MS both revealed the presence of many high molecular weight products which correspond in molecular weight to adducts of the PAH and one or



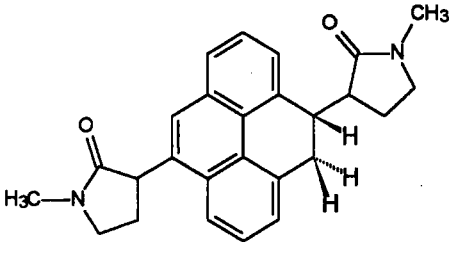
**1**

MW = 299



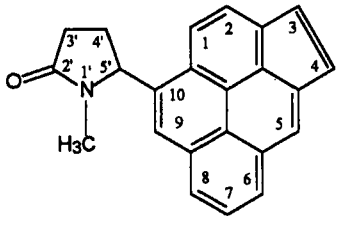
**2**

MW = 301

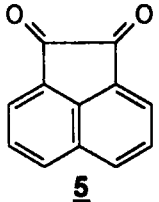


**3**

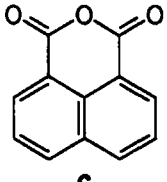
MW = 398



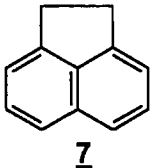
**4**



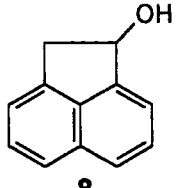
**5**



**6**



**7**



**8**

**Figure 5** Structural features of photoproducts.

more NMP molecules. Proposed structures for some of the products are shown in Figure 5. Two types of adducts were found using APCI/LC-MS, the first is illustrated in structure **1** and the second in structure **2**. Structure **1** was also detectable by GC-MS whereas structure **2** was not. Many structural isomers of these molecules are possible and it cannot be determined from the data at hand where the NMP molecule is attached to the PAH moiety and which atom of NMP is involved in bonding. The 3' and 5' positions are given as possibilities here.

*Cyclopenta[cd]pyrene*

As in the case of pyrene, the photooxidation of CPP led to a complex mixture of products. One of the major products consisted of a CPP molecule substituted with one NMP molecule as seen in structure **4** in Figure 5. This molecule was stable enough for GCMS identification.

*Mutation assay*

Product mixtures from each of the photooxidized PAH were tested for mutagenic activity using a *Salmonella typhimurium* forward mutation assay. None of the samples were found to be mutagenic in this assay. In addition, a number of products tentatively identified from the photooxidation of acenaphthylene were tested individually as reference standards. These included acenaphthene quinone (**5**), naphthalene-1,8-dicarboxylic anhydride (**6**), acenaphthene (**7**),1-acenaphthenol (**8**), naphthalene-1,8-carboxaldehyde, and naphthalene-1,8-carboxylic acid. All of these compounds were found to be nonmutagenic at levels up to 100 μg/mL.



*Acknowledgement*

This investigation was supported in part by National Institute of Environmental Health Sciences center grant NIH-5P30-ESO2109 and Health Effects of Fossil Fuels Utilization program grant NIH-5P01-ESO1640. The liquid chromatograph/mass spectrometry investigation was supported by Department of Energy grant DE-FG05-92ER7911. We thank undergraduate research investigators Aarti Sadwahni and Kevin Benjamin of M.I.T. and Sean Brown of Grambling U. for their assistance with the photooxidation experiments. We thank Andrew Schkuta for modifying our liquid chromatograph to permit computerized data acquisition.

*References*

1 G. Prado, P. R. Westmoreland, B. H. Andon, J. A. Leary, K. Biemann, W. G. Thilly, J. P. Longwell and J. B. Howard, in: *Chemical Analysis and Biological Fate: Polynuclear Aromatic Hydrocarbons [Proceedings, Fifth International Symposium on Polynuclear Aromatic Hydrocarbons]* ( M. Cooke, A. J. Dennis, eds., Battelle, Columbus, Ohio, 1981), pp. 189–198.
2. G. Grimmer, ed., *Environmental Carcinogens: Polycyclic Aromatic Hydrocarbons*, (CRC Press, Boca Raton, FL; 1983).
3. M. L. Lee, M. V. Novotny and K. D. Bartle, *Analytical Chemistry of Polycyclic Aromatic Compounds;* (Academic Press, New York, 1981).
4. D. A. Kaden, R. A. Hites and W. G. Thilly, *Cancer Res.*, **39**, 4152–4159 (1979).
5. P. P. Fu, F. A. Beland and S. K. Yang, *Carcinogenesis*, **1**, 725–727 (1980).
6. A. L. Lafleur, J. P. Longwell, P. A. Monchamp, L. Shirname-More, W. A. Peters and E. F. Plummer, *Energy & Fuels*, **4**, 307–319 (1990).
7. A. W. Wood, W. Levin, R. L. Chang, M. T. Huang, D. E. Ryan, P. E. Thomas, R. E. Lehr, S. Kumar, M. Koreeda, H. Akagi, Y. Ittah, P. Dansette, H. Yagi, D. M. Jerina and A. H. Conney, *Cancer Res.*, **40**, 642–649 (1980).
8. T. D. Behymer and R. A. Hites, *Environ. Sci. Technol.*, **19**, 1004–1006 (1985).
9. A. Hase, P. H. Lin and R. A. Hites, in: *Carcinogenesis, A Comprehensive Survey, Vol 1.: Polynuclear Aromatic Hydrocarbons: Chemistry, Metabolism and Carcinogenesis*, (R. I. Freudenthal and P. W. Jones, eds. Raven Press, New York, 1976) pp 435–442.
10. R. W. Matthews, *J. Catal.*, **111**, 264–272 (1988).

11. R. W. Matthews, *Water Res.*, **24**, 653–660 (1990).
12. J. C. D'Oliveira, C. Minero, E. Pelizzetti and P. Pichat, *J. Photochem. Photobiol. A-Chem.*, **72**, 261–267 (1993).
13. A. Mills and S. Morris, *J. Photochem. Photobiol. A-Chem.*, **71**, 75–83 (1993).
14. A. Mills, R. H. Davies and D. Worsley, *Chem. Soc. Rev.*, **22**, 417–425 (1993).
15. M. A. Fox and S. Olive, *Science*, **205**, 582–583 (1979).
16. W. A. Korfmacher, D. F. S. Natusch, D. R. Taylor, G. Mamantov, and E. L. Wehry, *Science*, **207**, 763–765 (1980).
17. A. L. Lafleur, Y. Nakagawa, *Fuel*, **68**, 741–752 (1989).
18. T. R. Skopek, H. L. Liber, J. J. Krolewski, and W. G. Thilly, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 410–414 (1978).
19. T. R. Skopek, H. L. Liber, D. A. Kaden and W. G. Thilly, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 4465–4469 (1978).
20. K. Hashimoto, T. Kawai, and T. Sakata, *J. Phys. Chem.*, **88**, 4083–4088 (1984).
21. S. Morris, Ph. D. Thesis, University of Wales, 1992.
22. S. Das, M. Muneer, and K. R. Gopidas, *J. Photochem. Photobiol. A-Chem.*, **77**, 83–88 (1994).
23. R. Livingston and K. S. Wei, *J. Phys. Chem.*, **71**, 541–547 (1967).
24. K. S. Wei, and R. Livingston, *J. Phys. Chem.*, **71**, 548–549 (1967).
25. K. A. Muszkat and S. Sharafi-Ozeri, *Chem. Phys. Lett.*, **38**, 346–348 (1976).