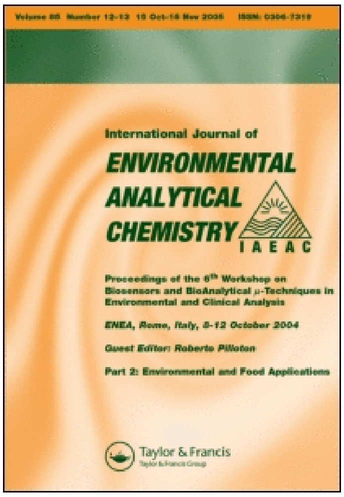

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STUDIES OF THE PHOTOCHEMICAL DEGRADATION KINETICS OF BaP ON DIFFERENT SUBSTRATES: FORMATION OF OXYGENATED COMPOUNDS*

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The rate constant for BaP decomposition induced by exposure to UV rays and rate constants for BaP1,6; 3,6; 6,12 diones formation were determined. Experiments were conducted by depositing the BaP on clean glass fiber-filter and on airborne particulate collected by filter. The BaP half-life appears to be positively correlated with filter loading and airborne particulates protect BaP from UV degradation. Our results suggest that BaP1,6dione, BaP3,6dione, BaP6,12dione are not the main by-products of BaP photodegradation induced by UV.

KEY WORDS: BaP, BaP photodegradation, BaP1,6dione, BaP3,6dione, BaP6,12dione, PAH.

INTRODUCTION

Polynuclear Aromatic Hydrocarbons (PAH) are widespread pollutants in the atmosphere, produced by high-temperature reactions such as incomplete combustion and pyrolysis of fossil fuels and other organic materials.

Knowing the mechanism of chemical reactions of PAH in the atmosphere is important because these reactions may represent a major mode of PAH decay, in addition to this some products of these reactions may be health hazards themselves being more toxic than PAH.[1,2]

According to experimental results, PAH degradation appears to depend on several physical and chemical parameters such as spectral composition and intensity of light, composition and physical characteristics of adsorbing matter (specific surface, particle size) and also on the presence and concentration of reactive gases (O_3, NO_x).[3]

PAH absorb ultraviolet radiation strongly at wavelengths of 300–420 nm (present in solar radiation at ground level), and most of them are very readily photo-oxized.[4] Some oxygenated compounds derived from PAH degradation have been found in the atmosphere, and the oxygenated fractions of several air extracts appear to be carcinogenic.[5–7]

Several investigations have shown that PAH are metabolized in mammalian

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Table 1 Characteristics of HPLC analysis

Instrument	Beckman model 421 A Controller and Model 110 B Solvent Delivery Module with a Altex 210 A Valve with a 50 ul loop
Column	Beckman Ultrasphere TM ODS 5 u, length: 25 cm; diam.: 4.6 mm
Solvent	CH3-OH, H20 (90:10)
Flow	0.5 ml/min
Detector	Beckman System Gold Scanning Detector model 167, wavelength: 254 nm
Integrator	Perkin Elmer Sigma 10

cells being finally stable products polycyclic quinones.[8,9] Moreover, in the literature it is reported that diones are the main by-products of the PAH photodegradation reactions.[3,10]

The aim of our work is to quantify the quinones formed by the photodegradation reaction of BaP adsorbed on solid substrates and exposed to UV rays and to determine the kinetics of this reaction.

MATERIALS AND METHODS

The BaP standard was obtained from Eastman Kodak CO. (USA), the BaP1,6dione; BaP3,6dione and BaP6,12dione were obtained from IIT research Institute (USA).

Airborne particulate, from urban areas, was obtained by filtration using glass fiber-filters (Gelman type A/E) conditioned at 400 °C for 1 hour before use and placed in a high-volume sampler (Metal Work GMWL 2000). Two samplings were carried out for 12 and 24 hours, at a flow rate of about 80 m^3/hr, to have two different dust-filter loadings: 0.23 and 0.69 mg/cm^2 respectively.

Using a hollow punch, disks (3.64 cm in diameter) were cut from the dust loaded and clean filters. The disks obtained from dust loaded filters were extracted with dichloromethan by soxhlet for 14 hours, to wash out the organic-soluble matter. Each disk was spiked with 200 ul of methanol containing 2.75 ug/ml BaP. After solvent evaporation, which required about 30 min, spiked filters were exposed, at a distance of 10 cm, to UV rays produced by a 15-watt unfiltered quartz lamp for a time ranging from 60 to 300 min. A set of unexposed spiked samples were used as controls. After exposure, each sample was placed into a conical vial and 1.5 ml of methanol containing 320 ng of 3,6-dimethylphenanthrene was added as an internal standard for quantitative analyses. The samples were sonicated in a water bath at room temperature for 5 min and then centrifuged at 2000 rpm for 5 min. The solutions were transferred to other vials and analysed by HPLC, whose experimental conditions are summarized in Table 1.

Identification of separated compounds was carried out by comparison with the retention times of standards. The quantity of BaP and of quinones was determined by using calibration curves obtained from the analysis of mixtures of known concentrations of the four compounds. The mean recoveries of the four components were: BaP: 82%; BaP1,6dione: 85%; BaP3,6dione: 85%; Bap6,12dione: 87%.

To check for possible losses of BaP due to sublimation or in the dark reactions, suitable amounts of this compound were deposited on clean filters, stored in the dark and analysed after 300 min. The recovery of BaP was of the same order of that determined in the calibration curves (83%, 3 independent experiments).

The efficiency of extraction of diones was checked using solvents of different polarity (cyclohexane, toluene, methylene chloride, aceton, methanol). Methanol and aceton were shown the highest dione recoveries (83–88%). However when adsorbed on airborne particulate the dione recoveries appeared to decrease strongly (from 20 to 50%).

To evaluate the rate of degradation of the tested diones due to UV rays, 0.20 ug of each dione was deposited on clean filters and exposed to UV rays, in the same experimental condition used for BaP. The extraction and analysis were carried out as previously described.

The concentration of O_3 in the air near the samples during the exposition time was evaluated using the colorimetric alkaline-KI method sugested by NIOSH (method No. P&CAM 154). The concentration remained very low (0.05 ppm) during the entire exposition times; therefore under experimental conditions significant effects induced by the presence of this powerful oxidant may be excluded.

RESULTS AND DISCUSSIONS

The BaP deposited on the clean glass-fiber filters and exposed to UV radiation was rapidly decomposed. The decay reaction follows an apparent first-order kinetics, and the experimental data fitted fairly well the equation:

$$\ln\,[\mathrm{BaP}]_t = \ln[\mathrm{BaP}]_0 - kt \text{ (Figure 1)}$$

where $[\mathrm{BaP}]_0$ = initial amount, $[\mathrm{BaP}]_t$ = amount present on the filter at time (t), K = decay constant. The BaP half-life was evaluated by equation:

$$t\tfrac{1}{2} = \ln 2/k.$$

Also the decomposition of BaP, deposited on airborne particulate matter appears to follow a first-order kinetics (Figure 1). In Table 2, the BaP half-lives, computed in different experimental conditions, are reported.

BaP half-life appears to decrease with increasing particulate load on filters. The statistical differences between these values were computed according the Mann-Witney U test.[11] The half-lives calculated for BaP exposed on loaded filters are statistically different from the values obtained using clean filters ($p = 0.028$); the two types of dust loaded filters show a low but significant difference ($p = 0.050$). These data are in agreement with our previous experiments[12,13] that had shown a shorter half-life of PAH exposed to sunlight when these compounds were adsorbed on airborne particulate matter.

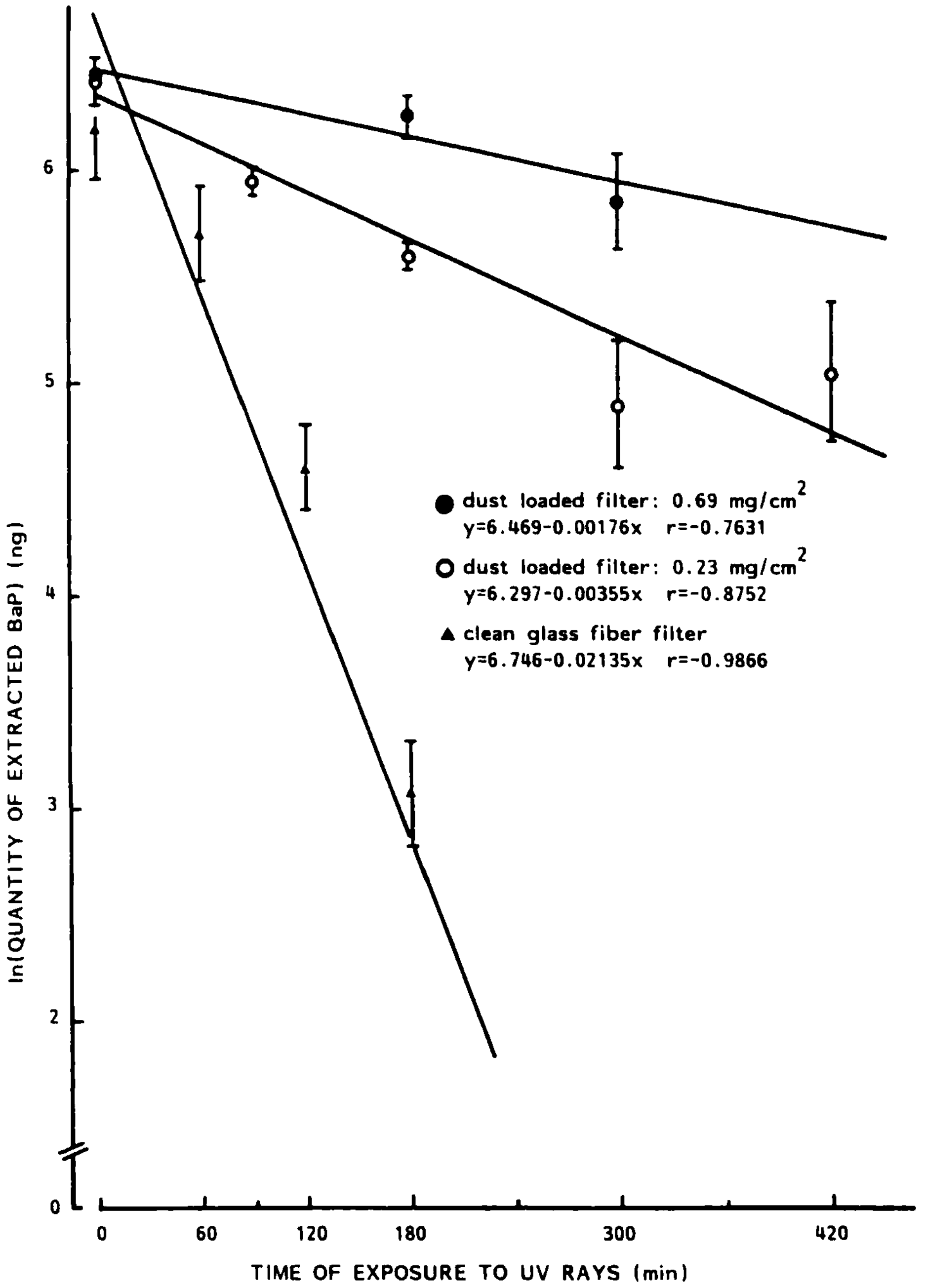

Figure 1 Decay of BaP deposited on different substrates exposed to UV rays. The points represent the mean ± SD of 3–4 independent experiments.

Table 2 Half-life and kinetic constant of BaP adsorbed on different filters and exposed to UV lamp

Experimental condition	*K (min-1)*	*BaP half-life (min) [mean ± SD]*
Dust loaded filters 0.69 mg/cm2	0.00176	428 ± 124
Dust loaded filters 0.23 mg/cm2	0.00355	199 ± 31
Clean filters	0.02135	37 ± 10[a]

Note: the values are the means of 3 and 4 experiments for dust loaded filters and clean filter respectively.

[a] Value statistically different from those obtained using dust loaded filters ($0.02 < p < 0.05$ Mann-Witney U test).

Table 3 Concentration of BaP and BaPdiones during exposure to UV rays (adsorbing substrate: clean glass fiber filter)

Exp. time (min)	*BaP (ng)*	*BaP1,6dione (ng)*	*BaP3,6dione (ng)*	*BaP6,12dione (ng)*
0	503.6 ± 125.8	nd	nd	nd
60	302.7 ± 58.7	2.9 ± 1.2	2.1 ± 1.1	9.9 ± 1.4
120	98.9 ± 21.3	12.6 ± 1.8	9.8 ± 2.2	18.7 ± 1.2
180	22.6 ± 5.6	23.4 ± 2.3	17.9 ± 2.0	24.9 ± 4.3
300	nd	24.8 ± 4.5	24.0 ± 6.3	20.5 ± 2.7

Note: the values reported are the mean ± SD of the quantity of extracted compounds in four independent experiments.
nd: Not detectable

Table 4 Regression lines of decay reactions of the diones exposed to UV rays

Compounds	*Regression equation*	*r*	*Apparent t1/2*
BaP1,6dione	$y = 5.152 - 0.01638x$	−0.9798	42.32 min
BaP3,6dione	$y = 5.315 - 0.02008x$	−0.9823	34.52 min
BaP6,12dione	$y = 5.510 - 0.02040x$	−0.9725	33.98 min

Note: $y = \ln(\text{dione detected})$ (ng); x = exposure time to UV rays. The equations represent the mean of 3 independent experiments.

In Table 3, the results of the effects of UV exposure on BaP deposited on a clean filter are reported. During the first 180 min there is a rapid increase of their concentration and the rate of formation appears to be constant in time. At exposure time of 300 min, when BaP results to be completely decomposed, degradation of the same diones, particularly BaP6,12dione, occurs. This result is in agreement with the fact that the same diones exposed to UV rays undergo photodegradation. Also in this case the reaction kinetics is apparently of first order and BaP6,12dione shows the shortest half life (33.9 min) (see Table 4).

Comparing the number of nanomoles of BaP and of the three diones in the experimental system at different exposure times, it is possible to note that there was no stoichiometric correspondence (Figure 2). The number of molecules of diones that are formed during the degradation is less than those of BaP that were decomposed in the same time.

It was not possible to study the kinetics of quinones formation exposing to UV

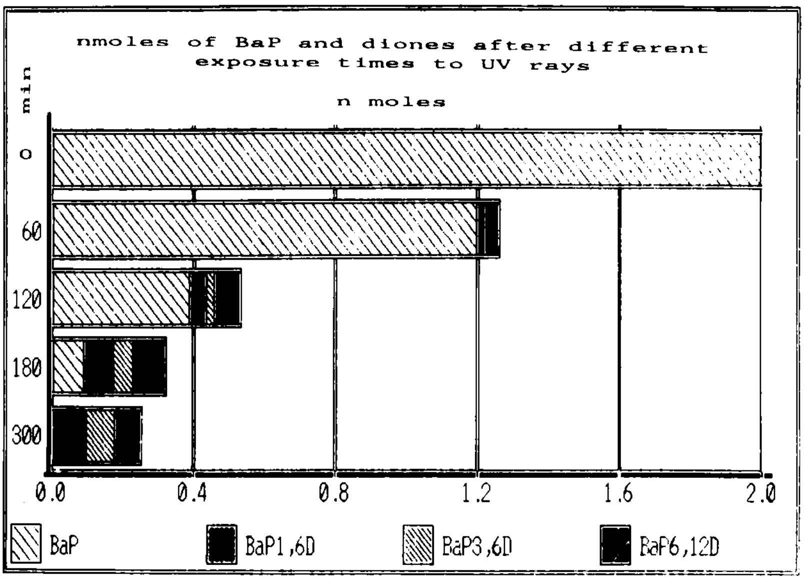

Figure 2 Mass balance of the photodegradation reaction of BaP.

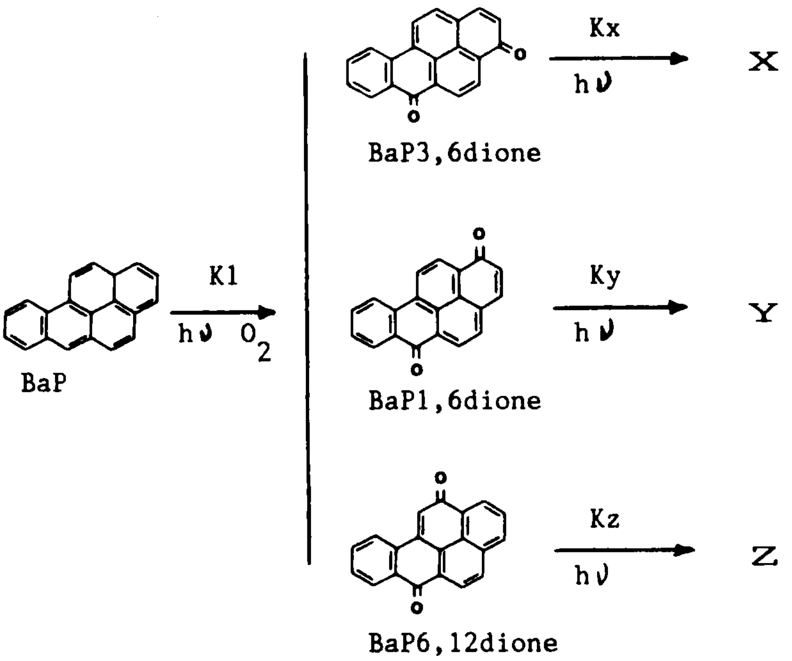

Figure 3 Schematic representation of the decay reaction of BaP. The determined value of decay constants are: Kl=0.02135; Kx=0.02008; Ky=0.01638; Kz=0.02040.

rays BaP adsorbed on airborne particulate. In fact, as previously described, the recovery of quinones adsorbed on airborne particulate resulted to be low, and therefore the amount of diones that was possible to extract in this experimental condition was under the minimum detectable value.

Our results show the complexity of degradation reactions of BaP. With our simple experimental model that considers only one chemical (BaP) and only one "degradation agent" (UV rays), the decay reaction at least involves two steps. BaP exposed to UV rays is transformed to three compounds (BaP1,6dione; BaP-3,6dione and BaP6,12dione) that are transformed by UV rays to other unknown chemicals.

The sequence of events induced on exposure of BaP to UV rays may be summarized as follows (Figure 3). The BaP, excited by UV rays (*hv*), reacts with atmospheric O_2, and diones are formed. These diones on exposure to UV rays undergo photodegradation with the formation of unknown chemicals, probably more oxidized compounds. The decay constant of BaP reaction and of the three diones degradation are of the same order of magnitude, so the quantity of each dione, detected in our experimental model, is determined by the ratios Kl/Kx; Kl/Ky; Kl/Kz respectively. The data obtained with our experimental approach seem to demonstrate that the complete photochemical decay process is the result of consecutive reactions.

Acknowledgements

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References

1. J. N. Pitt, *Ecotoxicol. Environ. Saf.* **2,** 199 (1978).
2. L. D. Claxton, *Environ. Mutagen.* **5,** 609 (1983).
3. K. Nikolaou, P. Masclet and G. Mouvier, *Science Total Environ.* **32,** 103 (1984).
4. National Academy of Sciences, Commitee on biologic effects of atmospheric pollutants: *Particulate polycyclic organic matter* Washington, DC (1972).
5. R. C. Pierce and M. Katz, *Environ. Sci. Technol.* **10,** 45 (1976).
6. A. J. Fatiadi, *Environ. Sci. Technol.* **1,** 10 (1967).
7. S. S. Epstein, N. Mantel and T. W. Stanley, *Environ. Sci. Technol.* **2,** 132 (1968).
8. A. Borgen, H. Darvey, N. Castagnoli, T. T. Crocker, R. E. Rasmussen and I. Y. Wang, *J. Med. Chem.* **16,** 502 (1973).
9. T. H. Maugh, *Science* **183,** 940 (1974).
10. R. A. Yokley, A. A. Garrison, E. L. Wehry and G. Mamantov, *Environ. Sci. Technol.* **20,** 86 (1986).
11. S. Siegel, *Nonparametric statistic for the behavioral sciences* (McGraw-Hill Book Company Inc., New York, 1956) pp. 312.
12. F. Valerio and A. Lazzarotto, *Intern. J. Environ. Anal. Chem.* **23,** 135 (1985).
13. F. Valerio, E. Antolini and A. Lazzarotto, *Intern. J. Environ. Anal. Chem.* **28,** 185 (1987).