Photolysis of polycyclic aromatic hydrocarbons in water

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PHOTOLYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER

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ABSTRACT

We have studied the photochemical reactions of eight polycyclic aromatics and heteroatom analogs (PAHs). Quantum yields and rate constants in sunlight and at single wavelengths were measured and half-lives of the PAHs as a function of the time of year were calculated. Product studies and the effect of humic acid and oxygen on rates are reported.

Introduction and Background

Emissions of mutagenic polycyclic aromatic hydrocarbons and their heteroatom analogs (PAHs) from processing and combustion of fossil fuels are widespread.[1] As a result, PAHs contaminate many surface waters[2] and bioaccumulate in several aquatic organisms.[3] This report describes photochemical studies performed on eight PAHs dissolved in water to obtain quantitative information on the rates of photolysis of aqueous solutions of these compounds in sunlight, their quantum yields at selected wavelengths, and some insights into the chemistry of the photoprocesses. Table 1 lists the chemicals and their relevant properties. Zepp and Schlotzhauer[4] recently reported similar studies with another set of PAHs.

In concurrent studies, other chemical, physical, and biological loss processes for these PAHs were investigated, and all of the kinetic and equilibrium data were combined in the multicompartment SRI model to provide a detailed fate assessment for each compound. Complete results are given in an EPA report by Smith et al.[6] For most PAHS discussed here, photolysis is a major transformation process in aquatic systems.

Experimental Method

Materials and chemicals--Humic acid (Fluka A.6) was purified by dissolution in 0.1N NaOH, centrifugation, filtration (0.45 μ) and reacidification with H^+-Amberlite ion exchange resin. Chemicals were purchased and purified as shown in Table 1. Pure water was obtained from a Millipore purification unit (reverse osmosis, activated carbon, ion-exchange, 0.22 μ filter) and gave no detectable dissolved carbon. Natural waters were drawn from Coyote Creek, San Jose, CA, Lake Tahoe, CA, and Searsville Pond, Stanford, CA; they were filter-sterilized (0.22 μ) and refrigerated. See Smith et al.[6] for detailed water quality parameters for these samples.

Table 1

PROPERTIES OF PAHs

PAHs[a]	Molecular Weight	Source/Purity (%)	Long Wavelength Absorption λ nm(ε/M^{-1} cm^{-1})[b]	Solubility, M[c,d]
Benz[a]anthracene (BA)	228	Eastman/90+	480(10)[h]	4.8(-8)[e]
Benzo[a]pyrene (BP)	252	Aldrich/99+	410(1100)[h]	4.8(-9)
Quinoline (Q)	129	Aldrich/99+[f]	340(9)[k]	4.7(-3)
Benzo[f]quinoline (BQ)	179	Eastman/95+	390(37)[k]	4.3(-4)
9H-Carbazole (CB)	167	Aldrich/99+[g]	380(12)[l]	6.2(-6)
7H-Dibenzo[c,g]carbazole (DBC)	267	Aldrich/96+	390(10)[k]	2.4(-7)
Benzo[b]thiophene (BT)	134	Aldrich/97+[g]	307.5(13)[k]	9.7(-4)
Dibenzothiophene (DBT)	184	Aldrich/95+[g]	340(13)	6.0(-6)

[a] Abreviations used elsewhere in text are parenthesized. [b] Noted for absorptivity values > 10 M^{-1} cm^{-1} at 2.5-10 nm intervals. [c] Measured by J. H. Smith and D. Haynes unless otherwise noted.[6] [d] Values in parenthesis are powers of ten. [e] Davis and Park.[5] [f] Purified by glc to 99+ % purity. [g] Recrystallized once to 98+ % purity. [h] In 50:50 AN/H$_2$O. [k] In water. [l] In 26:74 AN/H$_2$O.

Reaction solutions were prepared from stock solutions in acetonitrile (AN) to give final concentrations in 0.1%, or 1% AN in water at less than half the solubility limit of the chemical, typically less than 1 μg ml^{-1}.

Photolyses were performed on a merry-go-round reactor (MGRR--Ace Glass) with 400-w medium pressure mercury lamp filtered to give 313- or 316-nm bands or > 300-nm broad spectrum light. Reaction tubes were 10-mm-O.D. borosilicate tubes.

Photolysis--Solutions were photolyzed in the MGRR at 313 and 366 nm. Actinometry was performed at these wavelengths, using optically thick solutions of o-nitrobenzaldehyde at 313 and 366 nm (Pitts et al.[7]), Values of incident light intensity (I_0) were $\sim 1 \times 10^{18}$ photons ℓ^{-1} s^{-1} at 313 and 366 nm respectively. Photolyses were also performed in sunlight by exposing several solutions of each chemical at a fixed location facing south at 60° to the horizon. Most PAHs were analyzed by HPLC on a C18 reverse phase column; quinoline was analyzed by GLC, using 10% FFAP on A/W Chromosorb at 165°. In either kind of experiment, loss of a PAH was followed with time and the data were fitted to the first-order regression

$$\ln(C_o/C_t) = k_p t \qquad (1)$$

where C_o and C_t are the concentrations of PAH at times zero and t, k_p is the first order rate constant (sec^{-1}) and t is in units of seconds. In all but two cases good first-order behavior was noted. The quantum yield, ϕ, was calculated from the relation

$$\phi = k_p/2.3\varepsilon I_o r \qquad (2)$$

where ε is the molar absorptivity and r a reactor constant.

Results

Table 2 summarizes the results of photochemical studies performed on solutions of the eight chemicals listed in Table 1 in pure water or filter-sterilized natural waters with up to 1% acetronitrile or methanol at 23-28°C.

Because our primary interest in this study was to predict the rate of loss of these chemicals in sunlight, we used the quantum yields to calculate the rate constants, k_{pE}, and half-lives, $t_{\frac{1}{2}}$, for photolysis in sunlight as a function of time of year at 40°N latitude. These calculations are readily performed using a form of the relationship (Zepp and Cline[8])

$$k_{pE} = 2.3\phi r \Sigma I_{o\lambda}\varepsilon_\lambda \qquad (3)$$

where $I_{o\lambda}$ is the solar irradiance in the surface water in Einsteins liter^{-1} sec^{-1} at each wavelength where absorption is measurable. $I_{o\lambda}$ is defined as Z_λ for midday rates or L_λ for day-averaged rates by Zepp and Cline[8] and Mabey et al.,[9] respectively.

Calculations of k_{pE} at several times during the year were performed for each chemical, using values of ϕ measured in the laboratory (Table 2), ε_λ from spectral measurements (usually in acetonitrile solvent) and the computer program of Zepp and Cline,[8] or by hand, using the equation $k_{pE} = r\phi\Sigma\varepsilon_\lambda L_\lambda$, where L_λ is the day-averaged solar radiation flux factor at each wavelength interval where ε_λ is measurable (Mabey et al.[9]). Table 3 lists values of k_{pE} calculated

Table 2

PHOTOLYSES OF PAHS AT 313 OR 366 nm AT 23-28°C AND IN SUNLIGHT

PAH	Mol. Wt.	Initial Concentration (M)	Per Cent Conversion	λ nm	ϕ	k_p sec^{-1}	k_{pE} sec^{-1} (date)[e]	$t_{\frac{1}{2}E}$ (hr)	Cosolvent[f] (%)
BA	228	7.9(-8)	38,63	313	3.2(-3)	(2.28 ± 0.08)(-5)[a]	(5.91 ± 0.07)(-5)		1 AN
		8.6(-8)	67,83	366	3.4(-3)	(13.4 ± 0.7)(-5)[a]	E March	5	
BP	252	1.1(-6)	71	313	8.9(-4)	(1.05 ± 0.09)(-5)	1.79(-4) M Dec.	1.1	1-20 AN
		5(-8)	77,87	366	5.4(-4)	(3.86 ± 0.71)(-4)[a]	2.79(-4) L Jan.	0.69	
Q (pH 6.9)	129	6.3(-6)	42	313	3.3(-4)	(6.07 ± 0.00)(-6)	(7.7 ± 0.6)(-7)	25	--
		5.3(-6)	61	313	3.1(-4)	(5.84 ± 0.14)(-6)	L June		
BQ	179	4.1(-5)	39	313	1.4(-2)	(1.73 ± 0.15)(-5)	(1.4 ± 0.66)(-5) M June	14	1 MeOH
CB	167	6.0(-6)	85	313	7.6(-3)	(7.5 ± 0.18)(-5)	(6.59 ± 0.2)(-5) M Jan.	2.9	1 AN
DBC	267	3.4(-8)	15	313	--	1.8(-4)[b]	(5.18 ± 0.32)(-3)	0.037	0.1 AN
		3.4(-8)	84	366	2.8(-3)	(1.52 ± 0.10)(-3)	L Jan.	(2.2 min)	
BT (pH 6.9)	134	7.5(-6)	39	c	~0.1[d]	(3.5 ± 0.22)(-6)	(6.9 ± 0.7)(-6)	28	--
		7.5(-6)	84	c	~0.1	(5.12 ± 0.28)(-6)	L May		
DBT	184	2.7(-6)	60	313	5.0(-4)	(2.32 ± 0.22)(-6)	(2.04 ± 0.08)(-6) E March	94	1 AN

Note: Negative numbers in parentheses are powers of ten.

[a] Average of two experiments

[b] Initial rate only; reaction stopped after 15 minutes.

[c] Borosilicate filter to pass light > 300 nm.

[d] Estimated from rate in sunlight.

[e] E, M, L: early, mid, late

[f] Percentage of organic solvent in water: AN = acetonitrile

Table 3

CALCULATED AND MEASURED RATE CONSTANTS FOR PHOTOLYSIS OF AROMATICS IN SUNLIGHT AT 40° LATITUDE
(k_{pE} in sec^{-1})

PAH	Measured (season)	Winter[a]	Spring[a]	Summer[a]	Fall[a]	$k_{pE}^{Sum}/k_{pE}^{Win}$
BA[b]	6.0 x 10^{-5} (Spring)	1.4 x 10^{-4}	2.2 x 10^{-4}	3.8 x 10^{-4}	2.2 x 10^{-4}	2.7
BP[b]	1.8 x 10^{-4} (Winter)	1.8 x 10^{-4}	2.8 x 10^{-4}	3.9 x 10^{-4}	2.3 x 10^{-4}	2.2
Q[c]	4.0 x 10^{-7} (Summer)	5.0 x 10^{-8}	2.3 x 10^{-7}	3.6 x 10^{-7}	1.3 x 10^{-7}	7.2
BQ[b]	3.7 x 10^{-4} (Summer)	1.5 x 10^{-4}	2.4 x 10^{-4}	4.8 x 10^{-4}	2.0 x 10^{-4}	3.2
CB[b]	6.6 x 10^{-5} (Winter)	6.5 x 10^{-5}	1.0 x 10^{-4}	2.0 x 10^{-4}	0.9 x 10^{-4}	3.1
DBC[b]	5.2 x 10^{-4} (Winter)	2.3 x 10^{-4}	3.9 x 10^{-4}	5.0 x 10^{-4}	3.2 x 10^{-4}	2.2
BT[c]	6.9 x 10^{-7} (Summer)	2.3 x 10^{-8}	2.7 x 10^{-7}	5.7 x 10^{-7}	1.2 x 10^{-7}	25
DBT[c]	1.0 x 10^{-6} (Spring)	2.9 x 10^{-7}	1.1 x 10^{-6}	1.5 x 10^{-6}	9.1 x 10^{-7}	5.2

[a] Estimated from graphical output of computer calculation (Smith et al.[6]).
[b] Instantaneous rate constants at noon of December 21, March 21, June 21, and September 21.
[c] Averaged rate constant for a 24-hour day.
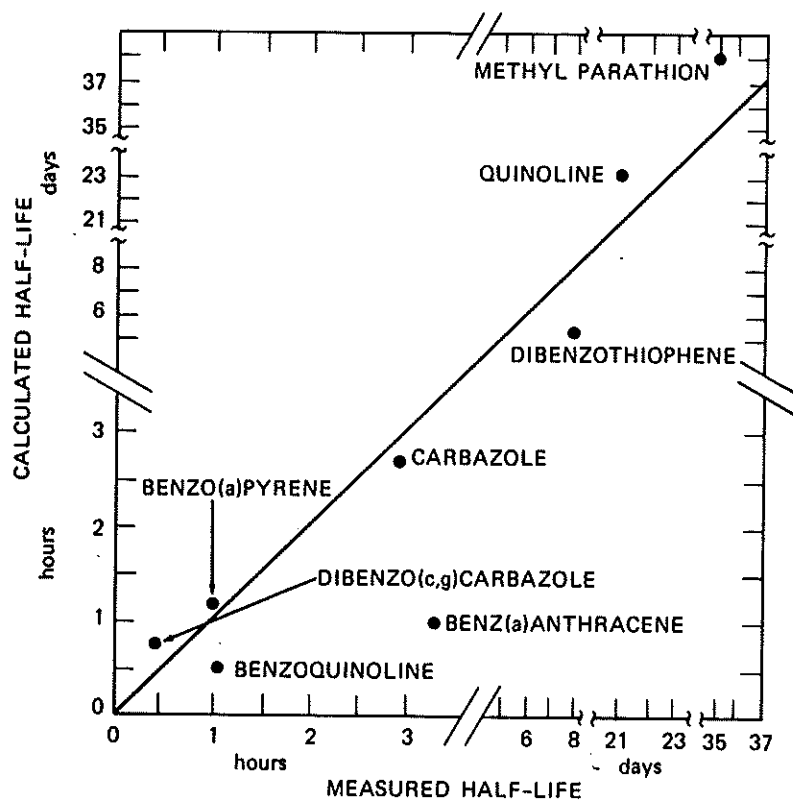
FIGURE 1   COMPARISON OF MEASURED AND CALCULATED HALF-LIVES
FOR DIRECT PHOTOLYSIS

for each chemical in the four seasons at 40° latitude, together with the measured value of k_{pE} on an indicated date. Rate constants in Table 3 were estimated either as instantaneous values at noon on the 21st of December, March, June, and September or averaged over a 24-hour day, depending on whether the half-life is substantially less or more than one day. In both cases the rate constants are maximum values expected under clear skies.

The last column of Table 3 gives the ratio $k_{pE}^{Sum}/k_{pE}^{Wint}$; the largest ratios are for quinoline and benzothiophene, both of which exhibit only weak tailing absorption spectra in the solar region above 290 nm. Figure 1 compares the calculated values with the measured values of k_{pE}. For most chemicals agreement is quite good; the largest differences are found for chemicals which photolyze in sunlight very rapidly, perhaps because of differences in spectra in water and in organic solvents where they were measured.

We investigated the effect of naturally occurring substances, such as humic acid and oxygen, on the rates of photolysis of these chemicals, using as solvents several natural waters drawn from oligotrophic and eutrophic sources, in addition to pure water. A variety of effects were found, including both inhibition and acceleration of rates by dissolved humic acid and oxygen. Tables 4 and 5 summarize some of the data obtained. Absorbance by the natural waters did not exceed 0.20 AU at 366 nm, which corresponds to less than 5% attenuation of light (light screening) over the 1-cm pathlength used in photolysis experiments. Absorbance by added humic acid (8 to 12 $\mu g\ ml^{-1}$) did lead to a 30-37% attenuation in light; on this basis one might expect similar reductions in rates. In fact, most aromatics exhibited much larger reductions in rate, indicating that both light screening and quenching occurred. However, on addition of humic acid, quinoline photolyzed much faster in sunlight, (but not at 313 nm) indicating that sensitization may have occurred.

The effects of oxygen on rate constants for photolysis were mixed: for DBT and DBC, nitrogen purge of the aqueous solutions had no significant effect on k_p; for BA and BP, purging with nitrogen strongly inhibited photolysis, whereas for BQ, purging oxygen markedly accelerated photolysis. No results are available for BT.

Some efforts were made to identify products of photolysis in aerated pure water. Only in the case of BP did we achieve complete product balance and identification. The photolysis of BP gives a 1:3 ratio of 3,6- and 1,6-BP quinones; only a trace of 6,12-quinone was found. These products were identified and quantified by HPLC,[10] using authentic samples provided by NIC/NIH.[11]

Other photolysis mixtures were analyzed at low conversion of PAH by HPLC and field ionization mass spectrometry (FIMS) with the following results:

BA--Three products were observed by HPLC, one of which, 7,12-BA quinone, accounted for 30% of the BA photolyzed. The two other products were not identified.

BQ--Photolysis in water gave two products which were not identified; we found different products when photolyses were performed in acetonitrile or methanol.

CB--We found seven major HPLC peaks on photolysis even at low conversions. FIMS on the mixture gave peaks of 171, 183, 197, 199, 332, 348 and 364 amu (CB has a peak at 197 amu).

Table 4

EFFECT OF HUMIC ACID ON PHOTOLYSIS RATES OF PAHs

PAH	Concentration(M)	λ, nm	Humic Acid Concentration or Source	k_p' [a] sec^{-1}	k_p'/k_p [b]
BA	9.6×10^{-8}	366	Coyote Creek	8.8×10^{-5}	0.66
		366	8 μg ml^{-1} HA	3.9×10^{-3}	0.29
BP	5.2×10^{-8}	366	Coyote Creek	1.7×10^{-4}	0.45
		366	12 μg ml^{-1} HA	0.69×10^{-4}	0.18
Q	5.3×10^{-6}	313	9.5 μg ml^{-1} HA	2.60×10^{-6}	0.38
	5.2×10^{-6}	sunlight[c]	9.5 μg ml^{-1} HA	3.0×10^{-6}	3.9
BQ	5.1×10^{-5}	313	8 μg ml^{-1} HA	0.28×10^{-5}	0.16
CB	6.0×10^{-6}	313	8 μg ml^{-1} HA	2.5×10^{-5}	0.33
		313	Coyote Creek	7.7×10^{-5}	1.0

[a]Rate constant in water containing humic acid.

[b]Ratio of rate constants in humic acid water and pure water.

[c]Late June

Table 5

EFFECT OF OXYGEN ON RATE CONSTANT FOR PHOTOLYSIS OF PAHs

PAH	Concentration, (M)	λ, nm	Ratio of k_p in Aerated and O$_2$-free Solutions[a]
BA	8.6×10^{-8}	366	0.3
BAP	5.0×10^{-8}	366	0.02
Q	5.2×10^{-6}	313	0.97
BQ	4.0×10^{-5}	313	1.7
C	6.0×10^{-6}	313	1.0
DBC	3.4×10^{-8}	313	1.0
DBT	2.7×10^{-6}	313	~ 1.0 [b]

[a]Values of k_p in aerated water were taken from Table 2.

[b]Values of replicate measurements in purged DBT solutions were erratic but close to (< 2x) that of aerated solution.

Tentatively, these peaks correspond to carbazole monomer and dimer with added hydrogen and oxygen.

DBC--Two primary products were found by HPLC analysis. Both products were separated by HPLC and subjected to FIMS. The only distinguishing features of the spectrum of the major product were an apparent molecular ion at 299 amu and peaks at 270 and 271 amu, corresponding to loss of CHO and CO, respectively, from the molecular ion; this indicates the presence of at least one phenolic group (McLafferty[12]). DBC itself has a molecular ion of m/e 267. The spectrum of the major product is compatible with that of a dihydroxylated DBC; however, no silylated derivative of this product could be obtained using O, N-bis(trimethylsilyl) trifluoro-acetamide. Since the values of k_p for CB and DBC were unaffected by purging of O_2 (see Table 5), we suggest that oxygen in products from these PAHs may have come from water, perhaps via a radical-cation intermediate.[13]

DBT--Photolysis gave five early-eluting, primary products in the HPLC analysis. Attempts to characterize these products using GC/MC were unsuccessful. However, when the reaction solution was degassed before photolysis, the yield of the third eluting product was diminshed, and that of the fifth eluting product was increased. These results suggest that both water and oxygen may be involved in some product-determining steps.

Discussion and Conclusions

The results shown in Tables 2 and 3 indicate clearly how rapid PAH photolysis is in sunlight; strong absorptivity in the solar spectrum by the higher molecular weight PAHs offset small values of ϕ and give $t_{1/2}$ values of a few minutes to a few hours. Seasonal effects on $t_{1/2}$ are only a factor of two or three from summer to winter, except for Q and BT, which absorb weakly in the solar region.

All of the quantum yields reported here are much less than one, indicating the overriding importance of competing processes that deactivate the excited state intermediate(s).

We find no obvious structure-quantum yield relations among the set of PAHs examined by us or by Zepp and Schlotzhauer.[4] For eight hydrocarbon PAHs containing two to five fused rings, ϕ varied only from 1.5×10^{-2} to 0.033×10^{-2}; O, N or S-heteroatom substitution in one to three ring PAH enlarged the range of ϕ from 0.1 to 0.33×10^{-2}. Substitution of N for C in napthalene to give quinoline, or S for C=C to give benzothiophene reduced ϕ by a factor of 10-20. Additional fused benzene rings, as in napthalene/anthracene, CB/DBC, tended to reduce ϕ, except for the pair anthracene/BA.

The small effects of humic acid and oxygen in most photolyses are surprising and indicate either that many of these photolyses proceed in singlet states or that the triplet states of these PAHs are too shortlived to be quenched by oxygen and too energetic to be sensititzed by humic acid. Zepp and Schlotzhauer[4] discuss the case of PAHs shielded from sunlight in absorbing natural waters and conclude that PAH will still photolyze rapidly in most marine and freshwater systems, in agreement with our observations. Using a computer model, we also have examined the effect on photolysis where there is strong sorption by some PAH to sediments (Smith et al.[6]).

The principal effect is to extend the time required to photolyze a significant fraction of the original PAH, because sedimentsorbed PAH (which presumably is not photolyzed) buffers the dissolved PAH and acts to restore the concentration in the water column as photolysis proceeds.

Acknowledgment

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