

Photochemical Sinks of Organic Pollutants in Estuarine and Near-Shore Environments

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Award Number: N00014-99-1-0034

<http://www.chem.umd.edu/ane/blough/index.html>

http://www.chem.umd.edu/organic/falvey/falvey_home.html

LONG-TERM GOALS

The principal objective of this work is to assess the quantitative importance of homogenous and heterogeneous photochemistry as a sink of pollutants in the aquatic environment. Using a combination of chemical trapping techniques, steady-state and time-resolved spectroscopic methods and product analysis, we are examining the mechanisms and magnitude of the photochemical production of strong oxidants and reductants by chromophoric dissolved organic matter (CDOM), as well as how these species may contribute to the degradation of common pollutants such as polycyclic aromatic hydrocarbons and halogenated organic compounds. The relative contributions of both the direct and sensitized photochemical destruction of these pollutant classes is under investigation. Ultimately, we hope to employ the information acquired from these studies to develop simple models that can be utilized to predict the photochemical rates of pollutant loss.

OBJECTIVES

Over the last year, our principal near-term objectives were as follows:

1. Prepare and publish a manuscript on the photoproduction of the hydrated electron (e^-_{aq}), a strong reductant, by humic substances and by CDOM in natural waters. A further objective of this portion of the project was to map the reduction potential of photogenerated species using a series of halogenated compounds having differing one-electron reduction potentials.
2. Prepare a manuscript on the aqueous photochemistry of 2-methyl-1,4-benzoquinone, a representative example of environmentally-relevant compounds capable of generating an oxidizing intermediate. Our future work will examine how quinone structure affects photochemical reactivity.

Report Documentation Page			Form Approved OMB No. 0704-0188		
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1. REPORT DATE 30 SEP 2001		2. REPORT TYPE		3. DATES COVERED 00-00-2001 to 00-00-2001	
4. TITLE AND SUBTITLE Photochemical Sinks of Organic Pollutants in Estuarine and Near-Shore Environments			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry and Biochemistry,,University of Maryland,,College Park,,MD, 20742			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
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15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a REPORT unclassified	b ABSTRACT unclassified	c THIS PAGE unclassified			

3. Initiate a detailed study of the mechanism(s) and magnitude of both the direct and sensitized photochemical destruction of polycyclic aromatic hydrocarbons (PAH's).

APPROACH

The first objective was achieved through the development of a two new chemical trapping methods (Thomas-Smith and Blough, 2001). The first employs the rapid reaction of N_2O with e^-_{aq} to form OH, followed by the reaction of OH with dimethylsulfoxide to generate a methyl radical, which is then trapped by an amino-nitroxide. Following derivatization with fluorecamine, the product is separated by reversed-phase high performance liquid chromatography (HPLC) and quantified fluorometrically (Kieber and Blough, 1990; Li et al., 1997; Vaughan and Blough, 1998, Li et al., 1999). The second employs the reaction of e^-_{aq} with monochloromethane to produce the methyl radical directly, which is then trapped by the nitroxide and analyzed as above. To examine the photoreducing potential of CDOM, the yields of carbon-centered radicals arising from the reductive dehalogenation of a series of chlorinated hydrocarbons with differing one-electron reduction potentials was determined by nitroxide trapping. Chlorinated compounds that are currently being examined include chloromethane, trichloromethane, 2-chloroethanol and chlorobenzene.

The second objective was achieved through a combination of laser flash photolysis studies and chemical trapping studies (Pochon et al., submitted).

The rates of the direct or sensitized loss of PAH's are being followed either by reversed-phase HPLC with fluorometric detection or by steady-state fluorescence. Product analysis is ongoing. PAH's that are currently being examined include anthracene, benz[a]anthracene, benz[a]pyrene, chrysene, pyrene, and perylene.

WORK COMPLETED

1. Published our work on the photoproduction of hydrated electron by humic substances and natural waters (Thomas-Smith and Blough, 2001; see abstract of article below that summarizes our findings). Extended our work on the characterization of other photoreductants produced by humic substances and natural waters.
2. Submitted a manuscript on our work investigating the aqueous photochemistry of benzoquinones. (Pochon et al., submitted; see abstract below that summarizes our findings).
3. Substantially completed a preliminary study on the rates of the direct and sensitized photochemical destruction of selected PAH's. This work is being prepared for publication (Fasnacht and Blough, in preparation).

RESULTS

The wavelength dependence for the photoproduction of the hydrated electron ($e^-_{(aq)}$) from various humic and fulvic acids and from natural waters was determined, employing a method that converts e^-_{aq} to a methyl radical which is detected fluorimetrically as the *O*-methylhydroxylamine of a stable nitroxide. Quantum yields for e^-_{aq} production from potassium ferrocyanide and *N,N* dimethylaniline are in agreement with previously reported values. The quantum yields for production of e^-_{aq} from chromophoric dissolved organic matter (CDOM), decrease precipitously with increasing wavelength

with the rate of decline increasing in the order: humic acid < fulvic acid < natural water in the UV-B region. For Suwannee River fulvic acid, quantum yields ranged from 7.9×10^{-6} at 366 nm to 1.9×10^{-4} at 296 nm indicating that previously reported values for e^-_{aq} production from CDOM involving laser sources of irradiation are high due to experimental artifact. Apparent natural water quantum yields at 296 nm are higher than those for humic substances, ranging from 9.4×10^{-5} to 3.7×10^{-3} depending on location. The highly absorbing waters of the Delaware and Chesapeake Bays show insignificant production of e^-_{aq} . These results indicate that the hydrated electron, through its reaction with dioxygen, is not a significant source of hydrogen peroxide in many natural waters and that humic substances may not be the principal source of e^-_{aq} production.

The above research has shown that e^-_{aq} is not the sole precursor of H_2O_2 in natural waters and that additional photoreductants capable of reducing dioxygen to superoxide (O_2^-) are being produced. To map the amount and reduction potential of these species, the photoreactions of a series of chlorinated compounds within Suwannee River fulvic acid (SRFA) and Shark River and Delaware Bay waters are being investigated. Conclusions to date are as follows:

1. Upper Chesapeake Bay water, which had previously been shown to produce little or no e^-_{aq} , produces photoreductants capable of reducing trichloromethane at wavelengths between 296 and 313 nm.
2. For a particular humic substance or natural water sample, the rate of photoreduction for a given chlorinated compound decreases with increasing wavelength, but the rate of decrease is more substantial for the natural waters.
3. For a given chlorinated compound, the product formation rate is higher for SRFA than for the natural waters.
4. For a particular humic substance or natural water sample, the product formation rates appear to increase with increasing ease of reduction of the chlorinated compound (production rates increase in the order, $CH_3Cl \leq ClCH_2CH_2OH < CHCl_3$).

Photolysis of 2-methyl-1,4-benzoquinone (toluquinone) in aqueous solution results in the oxidation of water to create either hydroxyl radical or some species capable of transferring a hydroxyl radical. Trapping of the latter with dimethyl sulfoxide (DMSO) creates a methyl radical which in turn can be trapped by the stable radical 3-amino-2,2,5,5-tetramethyl-1-pyrrolidinyloxy. Competitive trapping studies using DMSO and either nitrite anion or salicylate anion show that the hydroxylating species is much more selective in its reactions than free hydroxyl radical. Laser flash photolysis experiments on toluquinone in aqueous solution show formation of a transient species immediately (<150 ns) following the excitation pulse that had previously assigned to the excited triplet state of the quinone. This spectrum differs from the authentic triplet state spectrum generated in less reactive organic solvents (carbon tetrachloride and acetonitrile). The same intermediate is shown to react with the hydroxyl radical traps, cupric ions and benzoate anion to yield the semiquinone radical. On this basis of these experiments it is argued that this transient species is a hydroxylating intermediate, probably best described as a complex between the semiquinone radical and the hydroxyl radical. It is further argued that this species is responsible for the hydroxyl radical trapping reactions.

Our results on the direct and sensitized photochemical destruction of PAH's can be summarized as follows:

1. Quantum yields for the direct photochemical destruction of the PAH's examined are relatively high, $\sim 2 \times 10^{-3}$, and except for benzo[a]pyrene, did not vary by more than about a factor of two from this value.
2. Substantially lower rates of direct photolysis were observed at lower dioxygen concentrations for acenaphthene, benz[a]anthracene, benzo[a]pyrene, perylene and pyrene, clearly implicating O_2 in a photooxidation process. However, this result cannot be due to the direct reaction of 1O_2 with these compounds due to their very low concentration. It appears more likely a result of reaction(s) taking place within an excited state PAH- O_2 collision complex. In contrast, the loss of anthracene and chrysene showed little dependence on O_2 , suggesting the presence of an alternative reaction mechanism.
3. Except for anthracene, the loss of the PAH's was not enhanced in the presence of SRFA or in natural waters, indicating that the photosensitized destruction of these compounds is not important. Indeed, we observed up to a 2-fold inhibition in the rates of the direct photodegradation of some compounds in the presence of SRFA and natural waters.

IMPACT/APPLICATIONS

This work should allow us to gain a better understanding of the rates and mechanisms of the photochemical degradation of both natural and anthropogenic compounds in natural waters. This knowledge should, in turn, allow us to develop predictive models for the photochemical destruction of new compounds released to the environment.

TRANSITIONS

The radical trapping approach that we have continued to develop in this work (Thomas-Smith and Blough, 2001), was designed originally (with ONR support) as a highly-sensitive means with which to detect and identify radicals optically in environmental systems (Blough and Simpson, 1988). However, the use of this approach has expanded widely and now includes applications in the biological and health sciences (eg., Pou et al., 1993; Kalai et al., 1998; Hideg et al., 1998; Li et al., 1999a, 1999b, 2000, Lozinsky et al., 2001, Flicker and Green, 2001, Haugland, 2001) and polymer chemistry (eg., Gerlock et al., 1993; Moad et al., 1999; Ballesteros et al., 2001).

RELATED PROJECTS

In a related, ONR-supported project, we are examining the factors controlling the distribution and dynamics of CDOM in estuarine and coastal waters through a combination of field and laboratory measurements. As CDOM is the principal photoreactive constituent of most natural waters, an understanding of the factors that control its distribution in the environment is essential for determining the impact of photochemical processes in the mineralization of both natural and anthropogenic compounds.

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