In this investigation, phenolic compounds (phloroglucinol, cresol, 2,3-dimethylphenol, 2,3,5-trimethylphenol, and 2,4,6-trimethylphenol) were used at near-ambient concentrations to explore sea surface microlayer photochemistry. When solutions were irradiated with sunlight or ultraviolet light, first-order transformations of phenolic compounds such as phloroglucinol (PGL) were observed. The transformation rates were always faster in samples from organic-rich slicked surface microlayers than samples from subsurface bulkwater. Little transformation of phenols was observed in distilled water under sunlight irradiation. These results indicated that the phenols did not directly absorb sunlight to form photochemical products, but instead reacted with reactive transients that were photochemically produced from dissolved organic matter (DOM) chromophoric components. Trimethylphenol transformations were slower than those for phloroglucinol, but were faster than those for dimethylphenols and cresol, indicating that formation of phenoxides were important steps in phenol transformations. Transformation rate constants for PGL and cresol in the dark were less than 10% of rate constants in the light, indicating that microbial activity had little effect on transformations of these phenols.

Transformations of phenols in surface microlayer samples were accelerated by the addition of pterin as a photosensitizer, and with rates dependent on amounts of pterin added. Similar photosensitized transformations of natural phenols under natural sunlight are likely, with pterin or other nitrogen-containing heterocyclic compounds as an important group of natural photosensitizers in surface seawater.
Diagnostic tests using two singlet oxygen ($^{1}O_2$) quenchers and one free radical trapping agent, (NaN$_3$, 1,4-diazabicyclo [2,2,2] octane and 3-aminomethyl-2,2,5,5-tetramethyl-1-pyrroloidinyloxy, respectively) provided evidence that $^{1}O_2$ is the major transient that reacts directly with the phenols, with organic peroxy radicals (ROO·) less important. In oxygen-free conditions, transformation rates were slow, even with the addition of pterin as a photosensitizer, again indicating the importance of energy transfer processes involving oxygen molecules as energy acceptors. The measured first-order transformation rate constants of the phenols may actually have been pseudo first-order constants, dependent also on steady-state concentrations of $^{1}O_2$. Rate constants for transformations of the phenols with $^{1}O_2$ were estimated using $2 \times 10^{-14}$ M as a steady-state concentration of $^{1}O_2$ in surface microlayer samples. These results indicate that natural or pollutant phenols and other molecules are likely to undergo rapid photochemical transformations when they accumulate in surface slicks.
Photochemical Transformations of Phenolic Compounds
Added to Marine Surface Microlayers

by

Kaijun Lin

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PHOTOCHEMICAL TRANSFORMATIONS OF PHENOLIC COMPOUNDS
ADDED TO MARINE SURFACE MICROLAYERS

1. INTRODUCTION

The air-sea interface is important in many global chemical and geochemical cycles, because it covers 71% of the earth's surface and because all energy and material exchanged between atmosphere and ocean must cross the air-sea interface. In addition, many active and passive remote sensing data from air-borne and satellite instruments are collected from the interface itself or are modified by interfacial conditions. A wide variety of natural and anthropogenic materials, with hydrophobic moieties or associated with floatable particles, accumulate at the air-sea interface. High concentrations of many dissolved and particulate organic compounds, for example, have been found in samples collected from the air-sea interface (Hunter and Liss, 1977; Carlson and Mayer, 1980; Hardy, 1982; Henrichs and Williams, 1985; Williams et al., 1986). In order to assess chemical processes and rheological properties of the interfacial organic compounds, top layers of surface seawater are collected. These layers are called surface microlayers, and their thickness is dependent upon sampling techniques applied and upon research purpose (Garrett, 1965; Harvey, 1966; Harvey and Burzell, 1972; Baier et al., 1974; Hamilton and Clifton, 1979; Carlson, 1982a; Carlson, 1987).

At low wind speed (less than 5 m / s), some regions of the ocean surface appear smooth relative to adjacent surfaces, reflecting more sunlight back to the observer. It is generally believed that accumulation of organic compounds at the air-sea interface has significantly altered the surface elastic or rheological properties of seawater and modified the capillary wave spectra of the ocean surface, giving rise to such surface slicks. Although considerable effort has been made in the last decade, the chemical composition and structure of slicks are still not fully understood. Carlson and Carlson and co-workers (1980; 1982b) suggested that enrichment of ultraviolet-absorbing (280 nm) compounds in surface microlayers relative to subsurface waters could be used to indicate the presence of surface slicks. The ultraviolet-absorbing organic compounds, some of which are phenolic compounds, are important components of surface slicks and may be used as a predictive and comparative tool to further understand the source, structure and formation of surface slicks at the air-sea interface.
In the ocean, phenolic compounds usually occur as a consequence of natural decay processes (Julkunen-Tiitto, 1985). Other sources such as dry or wet deposition (Leuenberger, et al, 1985) or industrial activity (Throop, 1975; Leenheer et al, 1982; Goelitz et al., 1985) may be important in particular regions. Some even originate from microbiological degradation of nonionic surfactants present in detergents (Ahel and Giger, 1985). Phenolic and other organic compounds, after entering the marine environment, are involved in various chemical and physical processes that may significantly alter their characteristics. In these chemical and physical processes, photochemical reactions are important pathways for organic compound degradation, especially in the surface ocean. As slick components, phenolic and other organic compounds accumulate at the air-sea interface and receive a full surface spectrum of solar radiation. Significant photo-transformations can be expected in these slicks and their kinetics may be related to sinks and fates of the phenolic compounds in surface microlayers and related to the dynamics of surface slicks themselves. Knowing photo-transformation mechanisms of phenolic compounds may aid in understanding the amount and importance of photo-transients produced by sunlight-induced processes in surface microlayers, and may provide information about the source and the photo-transformed intermediate and end products of phenolic materials. Information about photo-produced intermediates, products and transients in surface microlayers may be relevant to understanding photochemical impacts on marine ecosystems generally.

The main objectives of this dissertation are: (1) to determine whether sunlight-induced transformations are a major removal pathway for phenolic compounds in marine surface microlayers; (2) to investigate the transformation kinetics of phenolic compounds and to estimate the residence times and half-lives of phenolic compounds in surface microlayers; (3) to understand the characteristics and mechanisms of photochemical transformations of phenolic compounds in surface microlayers; (4) to evaluate the importance of photo-induced photo-transients such as singlet oxygen ($^{1}O_2$) in marine photochemical processes.

1.1. SOLAR RADIATION AT THE SEA SURFACE

Solar radiation at the sea surface is significantly affected by absorption and transmission of sunlight through the atmosphere. In the atmosphere, sunlight is attenuated and scattered by water droplets and dusts, by gaseous molecules,
and by absorption by ozone. Because the ozone layer in the upper atmosphere strongly absorbs ultraviolet radiation, little radiation below 290 nm reaches the earth's surface so the spectral distribution of sunlight at the ocean surface is in the range of approximately 290 - 800 nm. As the surface sunlight penetrates the water column, its effects are primarily to heat the water mass and to drive photosynthesis. A part of the remaining sunlight is scattered and absorbed by suspended and dissolved organic and inorganic substances. These effects significantly attenuate the incident light intensity and alter its quality deeper in the water column. Thus, the under-water light field depends on transmission through the atmosphere, transmission through the air-sea interface, and optical properties of water column. In general, sunlight penetration is reduced to 1% of surface incident light at depths of 1 - 20 m near coasts and of 15 - 100 m in open oceans (Zafiriou, 1986). Very little light at effective wavelengths is available for photochemical reactions at or below these depths. In surface microlayers, however, water column attenuation effects are minimal. Therefore, solar irradiance in surface microlayers can be considered as equivalent to full surface solar radiation which depends on latitude, time of day, and season. Zepp and Cline (1977) developed a computer-model to calculate solar irradiance in surface natural waters and Zika (1981) calculated typical values of total solar irradiance at the sea surface in tropical areas of 3.2 * 10^25 photons m^-2 h^-1. Because surface microlayers are thought to be 100 - 200 µm thick or less, sunlight intensity and quality in surface microlayers can be simplified as maximal light intensity and full spectrum in comparison with underlying water.

Many chemical compounds are chromophoric, and photo-sensitive to radiation. Once these chromophores enter surface seawaters, photochemical reactions may occur due to solar radiation. Additionally, the accumulated chromospheric compounds in surface microlayers, especially in slicks, may absorb solar radiation directly and then initiate secondary photochemical transformations of chemical compounds that are not directly sensitive to solar radiation. For most chemical compounds in the marine environment, these secondary photochemical reactions are of primary importance. Due to the full sunlight intensity and spectrum, the higher concentrations of chromophoric compounds to initiate secondary photochemical reactions, and the accumulation of target compounds such as phenolic compounds, surface microlayers may be the most important photochemical reactors in the marine environment.
1.2. BACKGROUND OF THE SUNLIGHT-INDUCED PHOTOCHEMICAL PROCESSES IN AQUATIC SYSTEMS

Unlike conventional (e.g., laboratory) photochemistry, photo-induced processes in aquatic environments operate within a very complex environment: sunlight is a broad spectrum radiation with variable intensity; the aqueous medium may alter electronic states of organic compounds; many organic and inorganic components are resident in the reaction systems; and many variable environment factors affect the quantity and quality of light and reactants. The following discussion describes fundamental principles of aquatic environmental photochemistry.

1.2.1 Electronic Configurations

All photochemical reactions start with electronic excitation of molecules by light energy, and all undergo chemical reactions that may be thermodynamically unfavorable (i.e. $\Delta G_{\text{rxn}} > 0$) for molecules of unexcited ground states. The energy gained ($\Delta E$) by absorption of light satisfies negative free energy requirements (i.e. $\Delta G < 0$). Each excited state of a molecule has its own definite energy, life-time, and specific structure. An energy diagram is shown in Fig. 1.1 in which typical energy levels and electron jumps are portrayed. A ground state molecule, whose electrons occupy molecular orbitals of lowest energy, is excited by absorption of light energy to promote an electron to an antibonding orbital of higher energy that was not previously occupied by electrons. In fact, a simple molecule usually can have many excited states, but only the lowest excited states are usually considered because they have the longest life-times. They are respectively $n-\pi^*$ state ($n$ nonbonding to $\pi$ antibonding transition) and $\pi-\pi^*$ states ($\pi$ bonding to $\pi$ antibonding transition) according to Kasha's nomenclature (Horspool, 1976). The energy level of the $\pi-\pi^*$ state is higher than that of the $n-\pi^*$ state.

1.2.2 Electronic Multiplicity: Singlet vs. Triplet

In ground state, most molecules are in singlet state arrangement ($S_0$) with the spin of two electrons antiparallel. After excitation, if the promoted electron is still antiparallel to the electron in ground state, an excited singlet state ($S$) exists. If the promoted electron is parallel to the electron in the ground state, an excited triplet state
Figure 1.1. Relative energy of likely transitions in organic molecules. (Adopted from Horspool, 1976 without permission).
Figure 1.1.
(T) exists. Direct transition from $S_0$ to T is prohibited (Fig. 1.2), but T states may occur through intersystem crossing from singlet states. Mainly due to their molecular geometry, excited triplet states have lower energy levels and longer life-times than singlet states.

1.2.3. Radiationless Conversion and Radiation Conversion

Besides undergoing photochemical reactions, excited molecules may release their energy as heat or radiation. Radiationless conversion is an energy release process from high excited states to lower states in the same multiplicity (internal conversion) or different multiplicity (intersystem crossing). Due to longer life-times of the lowest excited states, intersystem crossing takes place only between the $S_1$ and $T_1$ (Fig. 1.2), and is a slow process relative to internal conversion. Radiation conversion is also an energy release process, in which light energy is emitted as excited molecules return to their ground states. Emission from $S_1$ to ground state $S_0$ is termed fluorescence and emission from $T_1$ to $S_0$ state is termed phosphorescence (Fig. 1.2).

1.2.4. Quantum Yield

Most excited molecules lose their energy rapidly instead of undergoing photochemical reactions. The photo-reacting efficiency of excited molecules is defined as the quantum yield ($\Phi$):

$$\Phi(\lambda) = \frac{N_{\text{rxn}}}{N_{\text{absorbed photons}}}$$  \hspace{1cm} (1.1)

In this equation, $N_{\text{rxn}}$ represents the number of excited molecules that undergo a chemical reaction, and $N_{\text{absorbed photons}}$ represents the total number of photons that are absorbed in the reaction system. The overall quantum yield of a photochemical reaction is a simple measure of light absorption efficiency of a chromophore to produce products via excited state (singlet or triplet), usually reflected in the magnitude of certain photo-induced processes. Quantum yields are affected by factors such as the nature of the chemical compound, incident wavelength, coexisting substances and environmental factors.
Figure 1.2. Modified Jablonskii diagram for photo-excited electronic multiplicity, and radiationless and radiation conversions (Adopted from Horspool, 1976 without permission).
Singlet manifold

Internal conversion

Intersystem crossing

Fluorescence

Phosphorescence

Figure 1.2.
1.3. Photochemical Processes at the Sea Surface

Because photochemical processes may affect the fate of organic compounds (natural and anthropogenic) in the marine environment, scientists have long been interested in seawater photochemical processes particularly near the surface. For example, removal mechanisms of oil films from natural waters via photo-induced chemical reactions have been suggested to be as important as microbial oxidation (Zika, 1981). Photo-transformations of various organic pollutants in natural waters have been most studied. Examples were given by Zepp and Baughman (1978) and Choudhry (1981). Because these photochemical reactions were only related to solar radiation, quantum yields, and the concentrations of the compounds, first-order reactions were often observed in natural waters. Detailed first-order kinetics of organic pollutants in natural waters were described by Leifer (1986).

A fraction of the components of naturally occurring dissolved organic materials (DOM) usually exhibit strong absorbance of solar radiation. These compounds are defined as DOM chromophoric components to solar radiation. These chromophoric compounds, whose structures are still largely unknown, are involved in photo-transformations of themselves when exposed to solar radiation. As the photo-transformations of DOM chromophoric components take place, short-lived intermediate species may be generated which may be highly reactive towards many other organic compounds in natural waters. In this way, organic compounds that are not chromophores to solar radiation may still be involved in photo-induced processes by secondary reactions with photo-produced reactive species. Indirect photochemical reactions are probably predominant because organic compounds that are able to directly absorb solar radiation to undergo chemical changes are rare and their environmental concentrations are dilute. Many photochemical studies have focused on organic-rich freshwater but due to the matrix effects these results can not be readily extrapolated to seawater. However, the general background for direct and indirect photochemical reactions in both freshwater and seawaters are similar. These basic concepts of photochemistry in natural waters will be discussed in next section.

1.3.1. Direct Photolysis

Due to their chemical structures, some chemical compounds directly absorb solar radiation in the near ultraviolet and visible region (320-800 nm) in natural waters,
leading to chemical changes or transformations of the compounds after a period of irradiation. For example, some polychlorophenols in estuarine water are believed to undergo direct photolysis with transformation kinetics dependent upon environmental factors (Hwang et al., 1986). Mechanisms for direct photolysis of compounds such as haloarenes may involve loss of their halogen substituents under ultraviolet radiation to form products of nucleophilic-substitution (Wong and Crosby, 1979). Competition between reductive dehalogenation (halogen replacement by hydrogen) and nucleophilic-substitution may occur, depending on the solvents involved (Soumillion and de Wolf, 1981). Scheme 1 illustrates processes by which anion free radicals are formed from haloarene excited states and competitive reactions in which anion free radicals abstract hydrogen or are attacked by nucleophiles.

Scheme 1

\[
\begin{align*}
\text{Ar-X} \xrightarrow{\text{hv}} & \xrightarrow{1[A_{\text{X}}]} \xrightarrow{3[A_{\text{X}}]} \text{Ar}^+ + X^- \\
\text{Ar}^+ + \text{RH} & \rightarrow \text{AR-H} + R^- \quad \text{(Hydrogen Abstraction)} \\
\text{Ar}^+ + \text{Y}^- & \rightarrow \text{AR-Y} \quad \text{(Nucleophilic-Substitution)} \\
\text{AR-Y} & \rightarrow \text{AR-Y} \\
\end{align*}
\]

Triplet states of haloarenes have been also observed in forming anion free radicals. Simple homolytic cleavages of C-X bonds of triplet haloarenes, especially of C-I and C-Br bonds, are possible (Arnold and Wong, 1977; Bunce and Ravanal, 1977). However, haloarenes of triplet state may not have sufficient energy to directly cleave C-Cl bonds. Exciplexes formed between excited haloarenes and other electron donors such as amines have been proposed and documented (Bunce et al., 1976; Bunce, 1982; Bunce et al., 1982; Freeman et al., 1986); these reduce C-Cl bond breaking energy. In the absence of external electron donors, one haloarene molecule may serve as electron donor to form an excimer with another haloarene (Lui and McGlynn, 1976; Bunce et al., 1976). This excimer can eject both anion and cation radicals (Scheme 2).

Scheme 2

\[
\begin{align*}
\text{Ar-X} \xrightarrow{\text{hv}} & \xrightarrow{1[A_{\text{X}}]} \xrightarrow{3[A_{\text{X}}]} \text{Ar}^+ + X^- \\
3[A_{\text{X}}] + \text{Electron Donor (D)} & \rightarrow [\text{Ar-X}^{\cdots}D^+] \quad \text{(Exciplex)} \\
[\text{Ar-X}^{\cdots}D^+] & \rightarrow \text{Ar}^+ + X^- + D^+ \\
3[A_{\text{X}}] + \text{Ar-X} & \rightarrow [\text{Ar-X}^{\cdots}\text{Ar-X}^+] \quad \text{(Excimer)} \\
[\text{Ar-X}^{\cdots}\text{Ar-X}^+] & \rightarrow \text{Ar}^+ + X^- + \text{Ar-X}^+ \\
\end{align*}
\]
These mechanisms (Schemes 1 and 2), originally described in organic solvents, can still be applied to direct or indirect photochemical reactions in aquatic environments. Formation of free radicals in natural waters by solar irradiation of DOM or some particulate compounds are examples of direct photochemical reactions. The generation of free electrons or cation radicals by photo-ionization is a possible mechanism in seawater (Zafiriou, 1986).

1.3.2. Indirect Photochemical Processes

In aquatic environments, however, most chemical compounds are transparent to solar radiation and are not involved in direct photochemical reactions. They persist under solar radiation in pure water or "clean" natural waters or their sunlight-induced transformations proceed very slowly. It has been noted however that these compounds disappeared at significant rates under exposure to sunlight when humic substances or chromophoric organic components in "humic" substances were present, indicating that indirect photo-transformation may occur in natural waters that contain these chromophoric compounds. For example, ethylene thiourea was stable in pure water but apparently decomposed in organic-rich natural waters (Ross and Crosby, 1975). Although compounds such as ethylene thiourea (maximal absorption 240 nm) can not directly absorb appropriate wavelengths of solar radiation due to absence of radiation below 290 nm, other organic chromophores that absorb longer wavelengths of solar radiation may initiate secondary photochemical processes of these compounds via photo-produced species such as singlet oxygen (Kraljic and Kramer, 1978). Besides humic-like substances, other photosensitizers among the dissolved organic materials (DOM) are probably important sunlight chromospheres in initiating indirect photochemical processes in freshwater and seawater. The chemical composition and structure of chromophoric DOM components are still poorly understood, so difficulties are often encountered in determining the production of reactive species or the mechanisms by which secondary reactions occur.

As sunlight arrives at the sea surface, chromophoric components of DOM may absorb solar radiation of near ultraviolet and blue wavelengths (320 - 480 nm), resulting in excited states of these components in the ocean. In general, these sunlight-excited DOM components, especially those of large molecular weight, may (1) donate their energy to other chemical compounds and make them reactive; (2) transfer their electrons to other chemicals or eject an electron; (3) combine radicals
and result in incorporation of smaller reactive molecules into humic-like substances (e.g. Cooper et al., 1989). Because seawater, especially aerobic surface seawater, contains high concentrations of dissolved oxygen (ca. 10^{-4} M), excited DOM components may also interact with oxygen molecules or other excited DOM components in energy or electron transferring processes or in chemical processes that lead to the formation of so-called reactive photo-transients (reactive intermediates). Many oxygen-evolved photo-transients have been observed in natural waters that are very reactive for subsequent oxidation of organic compounds. The major photo-transients in natural waters are as follows: (1) singlet oxygen (\textsuperscript{1}O\textsubscript{2}) (Zepp et al., 1977; Wolff et al., 1981); (2) hydroxyl radical (\textsuperscript{OH}) (Zafiriou, 1974; Mill et al., 1980); (3) superoxide anion radical (O\textsubscript{2}\textsuperscript{-}) (Larson et al., 1981; Cooper and Zika, 1983); and (4) organic peroxy radicals (ROO\textsuperscript{•}) (Ross and Crosby, 1975; Mill et al., 1980). Other potential photo-transients may also occur in natural waters under solar radiation. Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), although not a transient due to its relative high stability in natural waters, is a secondary product of sunlight-induced reactions in natural waters (Cooper and Zika, 1983; Cooper et al., 1988). Hydrated electrons (e\textsubscript{aq}\textsuperscript{-}) (Fischer et al., 1985; Zepp et al., 1987) have been also identified in natural waters and may react with dissolved oxygen to form superoxide anion radical and with other chemical compounds (Ross, 1975; Fischer et al., 1985; Zepp et al., 1987). Although their steady-state concentrations in surface waters are not very high, these photo-transients are very reactive toward organic compounds that do not directly absorb solar radiation. The following discussion will focus on the detailed processes of sunlight-induced formation of these photo-transients and their reactions with other organic compounds in seawater and fresh waters.

1.3.2.1. Singlet Oxygen

Because of its relatively long life-time (2-4 microseconds) in aqueous solution (Merkel and Kearns, 1972; Scully and Hoigne, 1987), singlet oxygen (\textsuperscript{1}O\textsubscript{2}) has been considered the most common reactive photo-transient in natural waters and reactions of singlet oxygen with certain organic compounds are thought to be a widespread phenomena in sunlit natural waters (Zepp et al., 1977; Larson, 1978; Wolff et al., 1981). The source of \textsuperscript{1}O\textsubscript{2} in natural waters is an energy transfer process (Type 2 Photosensitization) between appropriate organic components (namely, photosensitizers) and dissolved oxygen molecules. Humic substances (humic acids
and fulvic acids) in aqueous solutions or natural waters are one type of material able to act as natural photosensitizers in formation of \(^{1}\text{O}_2\) (Zepp et al., 1977; Zepp et al., 1985; Haag and Hoigne, 1986). Although humic-like substances are not major components of marine DOM, other DOM chromophoric components have been reported to photosensitize and to generate \(^{1}\text{O}_2\) in seawater under solar radiation (Momzikoff et al., 1983b). DOM molecular weight seems not to correlate with production of \(^{1}\text{O}_2\) (Haag and Hoigne, 1986), suggesting that macromolecule components are not prerequisites for production of singlet oxygen in natural waters. Organic compounds of low molecular weight, such as nitrogen-containing heterocycles, can photosensitize the formation of \(^{1}\text{O}_2\) in seawater. Examples include fluorescent pteridines and flavins (Joussot-Dubien and Kadiri, 1970; Chahidi et al., 1981; Momzikoff and Santus, 1981; Mopper and Zika, 1987). Pterins and flavins have been reported in seawater (Dunlap and Susic, 1985), so they may be active in marine organic photochemistry (Zafriou, 1977).

Under solar radiation, some chromophoric components of DOM may be photoexcited to form singlet states \((^{1}\text{DOM})\). Because singlet states are not stable, \(^{1}\text{DOM}\) goes, by intersystem crossing, to triplet DOM \((^{3}\text{DOM})\) of longer life-time and lower energy. \(^{3}\text{DOM}\) may then transfer its energy to dissolved molecular oxygen, although other competitive reactions proceed simultaneously (see sections 1.3.2.3, 1.3.2.4 and 1.3.2.6). A large fraction of photo-produced singlet oxygen will be quenched by water molecules or may decay to ground state by losing energy as heat. The process of these reactions is portrayed in Scheme 3 as follows:

\[
\text{DOM} \xrightarrow{hv} ^{1}\text{[DOM]} \rightarrow ^{3}\text{[DOM]} \\
^{3}\text{[DOM]} + \text{O}_2 \rightarrow ^{1}\text{O}_2 + \text{DOM} \quad \text{(Energy Transfer)} \\
^{1}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{Heat} \quad \text{(Major Sink)} \\
^{1}\text{O}_2 + \text{Organic Substrates} \rightarrow \text{Products}
\]

Recent research has indicated that \(^{1}\text{O}_2\) production depends on several factors including the type of photosensitizing components, the concentration of DOM, and the rate of sunlight absorption (e.g. Hoigne et al., 1989). In general, steady-state concentrations of \(^{1}\text{O}_2\) are proportional to the photosensitizing component content in DOM and the quantum yield of \(^{1}\text{O}_2\) production. The later decreases with increase of solar radiation wavelength for humic substances (Haag et al., 1984b). Steady-state
Concentrations of $^{1}{\text{O}}_{2}$ in several types of natural surface waters are $0.4 - 94 \times 10^{-14}$ M, with surface seawater at $10^{-14}$ M (Haag and Mill, 1989). In general, values for freshwater were higher than for seawater, presumably because the DOM content in freshwater is higher than in seawater. Because marine surface microlayers, especially surface slicks, are enriched with DOM and exposed to the full solar spectrum, a higher average value than $10^{-14}$ M is expected. But, the enriched DOM may also enhance quenching or other chemical processes.

Several classes of organic compounds can be oxidized by $^{1}{\text{O}}_{2}$ induced by ultraviolet radiation (Larson, 1978). In seawater, formation of carboxylic acids (Hansen, 1975) or formation of carbon dioxide, which indicates more complete oxidation (Armstrong et al., 1966), may be indicators of $^{1}{\text{O}}_{2}$ oxidation. Singlet oxygen is electrophilic and undergoes characteristic reactions such as cycloaddition reactions and "ene" reactions. Organic compounds of environmental interest such as cyclic 1,3-diienes, polynuclear aromatic hydrocarbons and phenols were suggested to react with $^{1}{\text{O}}_{2}$ in natural waters (Hoigne et al., 1989). Biological compounds such as some amino acids (histidine, tryptophan, tyrosine, methionine and cytosine), peptides, proteins, lipids and DNA also react with $^{1}{\text{O}}_{2}$ (e.g. Dahl, 1989). The importance of $^{1}{\text{O}}_{2}$ to environmental aquatic systems lies in its high reaction selectivity. Singlet oxygen has a longer life-time and a higher oxidation potential than of ground state oxygen molecule (22.5 Kcal / mol excess energy) in natural waters, but it may selectively react with electron-rich organic compounds (those with conjugated double bonds) within its diffusion radius (100 - 200 nm in pure water). For example, many phenolic compounds disappear under solar radiation in natural waters or aqueous solutions, and a group of alkylphenols were believed to undergo photo-oxidation by $^{1}{\text{O}}_{2}$ (Scully and Hoigne, 1987). Phloroglucinol under solar radiation in seawater was photochemically transformed to characteristic products of phloroglucinol polymers (Zika, 1977), indicating photo-condensation processes may occur in some cases. Others have suggested that humic substances are formed via photochemical processes (Harvey et al., 1983; Harvey and Boran, 1985), in which amino acids and lipids are precursors and $^{1}{\text{O}}_{2}$ plays a role in oxidation and cross-linking (Momzikoff et al., 1983a). Other possible $^{1}{\text{O}}_{2}$ involvement includes the photochemical transformation of trihydroxybenzenes into quinones as intermediate products, and a combination product, purprogallin, formed from pyrogallol (1,2,3-trihydroxybenzene) in aqueous solution (Perbet et al., 1982).

Direct evidence of photochemical reaction in natural waters via $^{1}{\text{O}}_{2}$ is still limited.
because the multi-component complexity of natural waters significantly affects reliable determinations. At present, the most effective approaches to test for $^1\text{O}_2$ mechanisms are additions of singlet oxygen quenchers that are able to physically quench $^1\text{O}_2$ in aqueous solution. Common quenchers are NaN$_3$ (Hasty et al., 1972; Haag and Mill, 1987) and DABCO (1,4-diazabicyclo [2,2,2,1] octane) (Quannes and Wilson, 1968; Zepp et al., 1977). Addition of these quenchers should slow photochemical reaction rates of target compounds or reduce product yields if $^1\text{O}_2$ is responsible for the reactions. Because life-times of $^1\text{O}_2$ are longer in D$_2$O than H$_2$O (Merkel and Kearan, 1972), accelerated photochemical reaction rates of target compounds in D$_2$O solution may also indicate the presence and importance of $^1\text{O}_2$ (Zepp et al., 1977).

1.3.2.2. Hydroxyl Radicals

In addition to $^1\text{O}_2$, sunlight-induced formation of other photo-transients is also very important in natural waters. Photo-produced free radicals have long interested scientists because they are very reactive toward organic compounds in natural waters. Among them, hydroxyl radical (OH·) is most oxidative (Dorfman and Adams, 1973) to most organic compounds. In natural waters, however, the actual formation of OH· remains unclear although it has been implicated in several studies of natural water photochemistry (Zafiriou, 1974; Mill et al., 1980; Zafiriou, 1983). In fresh waters, the formation of OH· appears upon slow photolysis of NO$_3^-$ / NO$_2^-$ (Haag and Hoigne, 1985; Zepp et al., 1987) (Scheme 4):

**Scheme 4**

\[
\begin{align*}
\text{NO}_3^- & \xrightarrow{\text{hv}} \text{NO}_2^- + \text{O}^- \\
\text{O}^- + \text{H}^+ & \rightarrow \text{OH}^-
\end{align*}
\]

\[
\begin{align*}
\text{OH}^- + \text{DOM} & \rightarrow \text{Unknown Products} \quad \text{(Major Sink)} \\
\text{OH}^- + \text{Organic Substrates} & \rightarrow \text{Secondary Reaction Products}
\end{align*}
\]

Direct photolysis of hydrogen peroxide may be a minor source of OH· production in natural waters (Haag and Hoigne, 1985). Additionally, other possible OH· sources are in consideration. In seawater, OH· appears to be formed on irradiation of marine DOM, as evidenced by correlation of OH· yields with DOM fluorescence (Zhou and Mopper, 1990). In upwelling areas of the ocean, NO$_3^-$ / NO$_2^-$ photolysis may be
also important in formation of OH\(^{-}\) (Mopper and Zhou, 1990). However, the mechanisms for OH\(^{-}\) formation from DOM in seawater are still unclear. Trace metals may be also involved in formation of OH\(^{-}\). For example, Cu\(^{+}\) and Fe\(^{2+}\) may be oxidized by hydrogen peroxide to contribute to OH\(^{-}\) pools in seawater (Moffett and Zika, 1987).

Because OH\(^{-}\) reacts with most organic compounds rapidly, DOM may play an important role in reducing OH\(^{-}\) production by quenching. However, it has been reported that steady-state concentrations of OH\(^{-}\) are proportional to nitrate-to-DOC ratios (Haag and Hoigne, 1985), reflecting the relationship between DOM and nitrate in production of OH\(^{-}\) in natural waters. Because of high reactivity of OH\(^{-}\) with DOM, low steady-state concentrations of OH\(^{-}\) are expected. Mill and his co-workers (1980) reported OH\(^{-}\) concentrations of 10^{-17} M in fresh water, several orders of magnitude lower than singlet oxygen. Although steady-state concentrations of OH\(^{-}\) are low, the high reactivities towards many organic compounds indicate an environmental significance. In some cases, they are even more important than \(^1\)O\(_2\) in natural waters.

In addition to reactions with organic compounds, OH\(^{-}\) reacts with bromide to produce Br\(_2^+\), a secondary free radical, and with HCO\(_3^-\) mediated by bromide to produce another secondary free radical, CO\(_3^+\) (Zafiriou et al., 1987) (Scheme 5):

Reactions to form secondary radicals may serve as a major sink (>90%) for OH\(^{-}\) in seawaters (Zafiriou, 1974; Zafiriou et al., 1987). In addition, combination of two OH\(^{-}\) leads to formation of hydrogen peroxide, making a contribution to occurrence of hydrogen peroxide in natural waters. Because OH\(^{-}\) may react directly with a wide variety of pollutants in natural waters, its application in pollution control and waste treatment can be extended. Possible mechanisms and products of phenols and a variety of other organic pollutants have been proposed by Cooper et al., (1990), although the source of OH\(^{-}\) was not from natural organic compounds in that case.
1.3.2.3. Organic Peroxy Radicals

Organic peroxy radicals (ROO·) are also important sunlight-induced photo-transients in natural waters (Mill et al., 1980; Larson et al., 1981; Zafiriou et al., 1990). Proposed mechanisms of formation of ROO· in natural waters (Haag and Mill, 1989) are presented in Scheme 6:

Scheme 6

\[
\begin{align*}
\text{DOM} \xrightarrow{\text{hv}} & \ 1[\text{DOM}] \\
1[\text{DOM}] & \rightarrow \text{DOM}^+ + \text{e}^- \quad \text{(Charge Transfer)} \\
\text{DOM}^+ + \text{O}_2 & \rightarrow \text{ROO}^· \\
\text{ROO}^· + \text{Organic Substrates} & \rightarrow \text{Reaction Products}
\end{align*}
\]

This mechanism of forming ROO· is based upon the charge transfer from DOM singlets to form a radical cation and the reactions of such radicals with dissolved oxygen molecules. However, only very small fractions of \(^1\text{DOM}\) (0.01%) may be involved in this process while large amounts undergo intersystem crossing to \(^2\text{DOM}\). Other sources of ROO· formation include the oxidation of reducing free radicals such as \(\text{R}^·\) and \(\text{RO}^·\) produced by homolytic cleavage (Zafiriou, 1986). Because of the unknown structure and chemical composition of DOM in natural waters, little attention has been focused on ROO· oxidation of organic compounds. Because the rates of radical cation production and of chain-propagating reactions with dissolved oxygen are poorly understood, the formations of ROO· and their detailed mechanisms need further investigation.

Because ROO· also have high reaction selectivity, quenching by DOM can be neglected. Decay processes for ROO· in natural waters are also less important in ROO· scavenging. Therefore, steady-state concentrations of ROO· are very high. In fresh waters, they were reported to be as high as \(10^{-9}\) M (Mill et al., 1980). Organic peroxy radicals may act as important photo-transients in photo-oxidation reactions with antioxidant compounds such as alkylphenols, aromatic amines, and thioiphenols (Anbar et al., 1973). A group of alkylphenols were photo-oxidized in fresh water samples, and ROO· were believed to be responsible photo-transients in these reactions, although no direct evidence was provided (Faust and Hoigne, 1987). In order to determine the involvement of ROO·, a new technique was developed by Kieber and Blough (1990) to measure the production of radical cations generated
by charge transfer of excited DOM in natural waters. The measurement was based on nitroxides, well-known carbon-centered radical trapping agents, that effectively reacted with photo-induced free radicals in solution (Blough, 1988). Nitroxides may also serve as a specific probe to test for photo-induced free radicals (probably radical cations) and possible involvement of ROO'.

1.3.2.4. Superoxide Anion Radicals

The presence of superoxide anion radical (O$_2^-$) has been demonstrated by several studies (Cooper and Zika, 1983; Zepp et al., 1986). When excited DOM ($^{1}$DOM) ejects electrons to form radical cations, dissolved oxygen molecules may receive the hydrated free electrons to reduce oxygen to O$_2^-$ (Soumillion and de Wolf, 1981; Haag and Mill, 1989) as shown in Scheme 7a. Other important possible mechanisms to form O$_2^-$ (Scheme 7b) involve direct charge transfer from excited DOM to oxygen molecules (Zepp et al., 1986). These two reduction processes differ in intermediate steps in which a caged complex is formed (Scheme 7a) and a photo-ionization process is involved.

\[ \text{DOM} \xrightarrow{\text{hv}} [\text{DOM}] \rightarrow [\text{DOM}]^+ + e^- (\text{Charge Transfer}) \]

\[ e^- + H_2O \rightarrow e_{aq}^- + O_2 \rightarrow O_2^- \]

\[ [\text{DOM}] + O_2 \rightarrow [\text{DOM}]^+ + O_2^- \]

\[ 2 O_2^- + 2 H^+ \rightarrow H_2O_2 + O_2 \quad \text{(Sink)} \]

Again, trace metals may play important roles in formation of O$_2^-$ in natural waters (Moffett and Zika, 1983; Sunda et al., 1983; Zepp et al., 1986).

Steady-state concentrations of O$_2^-$ have been estimated as $10^{-8}$ M in seawater depending on DOM content (Petasne and Zika, 1987), indicating that this sunlight-induced transient is potentially important in many reactions in natural waters. The recombination of two O$_2^-$ may lead formation of hydrogen peroxide (Scheme 7c) as an important sink for O$_2^-$ in seawater, and addition of superoxide dismutase (SOD)
accelerates this reaction. Therefore, SOD was suggested by Cooper and Zika (1983) to be used as a diagnostic agent for the presence of \( O_2^- \).

1.3.2.5. Hydrogen Peroxide

Hydrogen peroxide (\( H_2O_2 \)) may react directly with a wide variety of organic compounds (Plane et al., 1987; Zepp et al., 1986) or act as a source of free radicals (Zepp et al., 1977) even though it is rather stable compared with other photo-transients in natural waters. Also, as mentioned, measurement of \( H_2O_2 \) can be used as an indication for superoxide anion radical formation in natural waters. Photochemical formation rates of \( H_2O_2 \) are usually high in organic-rich natural water samples and vary with the concentration of dissolved organic substances. The solar spectrum seems also very important in production of \( H_2O_2 \) because the quantum yield of \( H_2O_2 \) formation apparently decreases with increasing wavelength (Cooper et al., 1988). In the ocean, concentrations of \( H_2O_2 \) vary with location, under-water light field, time of day, season, and mixing characteristics. In general, high concentrations of \( H_2O_2 \) are expected in coastal areas in surface water. \( H_2O_2 \) concentrations decrease with depth to below the detection limits at the base of the wind-mixed layer (Zika et al., 1985).

In natural waters, sunlight-induced \( O_2^- \) may act as a precursor which leads to formation of \( H_2O_2 \) (Cooper and Zika, 1983). Petasne and Zika (1987) showed that 70% of \( O_2^- \) in coastal seawater samples reacted to form \( H_2O_2 \), while 30% reacted to form unknown products. Scheme 7(c) demonstrated the formation mechanisms of \( H_2O_2 \) from \( O_2^- \) in natural waters. Other possible sources of \( H_2O_2 \) include photochemical or biological production or wet or dry deposition (Cooper et al., 1989).

1.3.2.6. Hydrated Electrons

Hydrated electrons (\( e_{aq}^- \)) can be also considered as photo-transients in natural waters. Their presence in natural waters has been determined by flash photolysis and kinetic spectroscopy of natural water DOM (Fischer et al., 1985). Their formation may be based on photo-ionization of DOM, perhaps through a caged complex to eject free electrons as well as cation radicals. The postulated formation mechanism is demonstrated in Scheme 8:
As discussed in previous sections, $e_{aq}^{-}$ may effectively reduce dissolved oxygen to form $O_2^{•-}$ in natural waters. Due to high concentrations of dissolved oxygen and competitive reactions with the oxygen as major sink for $e_{aq}^{-}$, the steady-state concentrations of $e_{aq}^{-}$ are low ($1.2 \times 10^{-17}$ M) in organic-rich lake water (Hoigne et al., 1989). Therefore, significant reactions by $e_{aq}^{-}$ are unlikely in natural waters unless the concentrations of organic compounds are high.

1.4. ENVIRONMENTAL SIGNIFICANCE OF MARINE SURFACE MICROLAYER PHOTOCHEMISTRY

In addition to a wide variety of organic compounds, marine surface microlayers and naturally occurring slicks especially may contain high concentrations of contaminants (Marty and Saliot, 1976; Hardy et al., 1987a,b; Word et al., 1987). These contaminants vary from polychlorinated biphenyls (PCB's), chlorinated hydrocarbons, and petroleum-derived hydrocarbons to combustion-derived polynuclear aromatic hydrocarbons (PAH's) (Hardy, 1982). Enrichment factors of PCB's and pesticides in surface slicks can reach $10^6$ to $10^7$ (Seba and Corcoran, 1969; Ofstad et al., 1979).

The fate of these organic contaminants in marine surface microlayers remains unknown, although photochemical transformations can be expected to be important pathways. Studies on photochemical processes of these anthropogenic compounds in surface microlayers may reveal the fate, source and exchange rates of these compounds between atmosphere and ocean. In addition, photochemical kinetics may supply important information on potential blue shift of solar radiation on the earth's surface. For example, a 30 nm blue-shift of solar radiation would result in a doubled concentration of singlet oxygen in natural waters (Mill and Haag, 1989), which might quantitatively enhance the reaction rates of singlet oxygen or other photo-transients photochemical processes. It may be possible to establish correlations of potential

---

**Scheme 8**

\[
\begin{align*}
\text{DOM} & \xrightarrow{hv} 1[\text{DOM}] \xrightarrow{\cdot} 3[\text{DOM}] \\
3[\text{DOM}] & \xrightarrow{} 3[\text{DOM}^{-}\cdot e^{-}] \xrightarrow{} \text{DOM}^{+} + e^{-} \text{(Charge Transfer)} \\
e^{-} + \text{H}_2\text{O} & \xrightarrow{} e_{aq}^{-} + \text{O}_2 \xrightarrow{} \text{O}_2^{•-} \\
e_{aq}^{-} + \text{Organic Substrates} & \xrightarrow{} \text{Reaction Products} \\
e_{aq}^{-} + \text{O}_2 & \xrightarrow{} \text{O}_2^{•-} \text{(Sink)}
\end{align*}
\]
depletion of ozone layer in the atmosphere with the kinetics of photochemical reactions of specific probe molecules in surface microlayers. Reactive photo-transients have negative impacts on marine ecosystems even while destroying organic pollutants. For example, singlet oxygen is believed to react selectively with important biomolecules such as proteins (MaGtheson et al., 1975), lipids (Straight and Spikes, 1985) and nucleic acids and their components (Kawanishii et al., 1986), damaging plasma membranes, mitochondria and nuclei. Because surface microlayers are accumulation sites for microorganisms and eggs and larval stages of some invertebrates and fishes, the production rates, steady-state concentrations, and factors affecting photo-transients in surface microlayers may be extremely important for environmental photo-toxicity studies.

The chemical composition of surface slicks may be considerably different from subsurface water (Williams et al., 1986), which may result in different photo-induced transformation pathways and altered photochemical mechanisms in surface slicks. Rates of photochemical reactions in slicks also differ considerably from those in subsurface waters. Other accumulated surface substances, such as trace metals, may influence surface microlayer photochemical reactions (Moffett and Zika, 1983; 1987), and accumulated suspended particles (living and non-living) may absorb or scatter light, adsorb hydrophobic organic compounds, or catalyze chemical reactions on solid-liquid interfaces (Kormann et al., 1988; Faust et al., 1989). Another important influence on the ocean surface may come from the atmosphere, which can produce and deposit photo-produced free radicals onto the air-sea interface (Thompson and Zafiriou, 1983). Because tropospheric ozone may penetrate marine surface microlayers, direct photolysis of ozone to produce hydroxyl radicals (Peyton and Glaze, 1987) could destroy ozone and contribute to free radical pools in surface microlayers and the surface ocean.
2. PHOTO-INDUCED DEGRADATION OF TRACER PHENOLS
ADDED TO MARINE SURFACE MICROLAYERS

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2.1. Abstract

To determine photochemical reactivity of surface microlayer components and to estimate residence times of phenolic materials at the ocean surface, we evaluated photo-induced degradation of three tracer phenols (phloroglucinol [1,3,5-trihydroxybenzene], TMP [2,4,6-trimethylphenol], and cresol [3-methylphenol]) added to samples of surface microlayers and subsurface waters. When all samples were exposed to the same natural sunlight conditions, first-order degradation rates of phloroglucinol in microlayer samples from surface slicks were always faster than degradation rates in microlayer samples not from slicks or in samples from subsurface seawaters. TMP was less photo-reactive than phloroglucinol, probably because of its lower dissociation to phenoxide ion at seawater pH. Degradation rates of phloroglucinol and TMP in microlayer samples from surface slicks were depressed by the presence of 50 μM NaN₃, a common singlet oxygen quencher, suggesting the involvement of photo-induced singlet oxygen. Generally, degradation of cresol was slower than either phloroglucinol or TMP although it should have had a higher degree of dissociation than TMP at seawater pH; degradation of cresol in seawater may be not via singlet oxygen. Dark control experiments exhibited less than 10% decreases in tracer phenol concentrations, indicating that microbial activities had little effect on degradation of these phenols. Because photoreactivity in samples from surface slicks was generally much greater than in other samples, microlayer photochemistry can not be estimated by simply extrapolating near-surface reaction rates to surface light intensities.
2.2. INTRODUCTION

It is obvious that the ocean surface is exposed to more light, especially at higher-energy low wavelengths, than subsurface water. The surface of the ocean is also an accumulation zone for a variety of dissolved organic materials (e.g. Williams et al., 1986, and references therein). The combination of relatively high light intensities and relatively abundant potential light absorbing and reactive molecules in ocean surface microlayers should make them zones of enhanced and perhaps unique photochemical activity, but this assumption has not yet been tested. Surface slicks, regions where small surface waves have been smoothed, are especially rich in organic materials, including UV-absorbing organic materials (Carlson, 1982b, 1983; Carlson et al., 1988). One group of UV-absorbing compounds enriched in oceanic surface microlayers, phenols (Carlson and Mayer, 1980), have been shown to be photochemically active in other natural waters (Hwang et al., 1986; Faust and Hoigne, 1987; Scully and Hoigne, 1987). We investigated photo-induced degradations of tracer phenols in surface microlayer samples from slicked and nonslicked surfaces and in samples of near-surface waters to determine photo-reactivities of surface microlayer components, to estimate surface residence times for natural or contaminant photo-degradable materials, and to better understand surface microlayer roles in photochemical processes in the oceans.

We determined photodegradation rates of three phenols (phloroglucinol [1,3,5-trihydroxybenzene], TMP [2,4,6-trimethylphenol], and cresol [3-methylphenol]) added to surface and subsurface samples under natural surface solar irradiation. Microbial degradation was tested using dark control experiments under the same conditions as the irradiation experiments. We also used a singlet oxygen quencher, sodium azide (NaN₃), to investigate mechanisms of microlayer phenol degradation.

2.3. EXPERIMENTAL METHODS

Tracer phenols were added to samples of surface microlayers and of subsurface water. These samples were then incubated in quartz tubes in natural surface sunlight for several hours. After exposure to light, the phenols remaining in solution were converted to diazotized sulfanilic acid (DSA) derivatives, concentrated by solid phase extraction, and analyzed by HPLC.

Surface microlayer and subsurface seawater samples were collected from a large
(600 m²) shallow flow-through basin at the Hatfield Marine Science Center in Newport, Oregon in July 1988 and from two areas near San Diego, California: La Jolla Bay on 15 to 22 September and near San Clemente Island on 23 to 25 September of 1988. Surface microlayer samples off southern California were collected with an automated surface microlayer sampler (Carlson et al., 1988) deployed from the R/V Sproul. These surface samples and parallel subsurface samples were pumped through UV absorbance (280 nm) and fluorescence (chlorophyll a wavelengths) detectors to determine the surface enrichments of dissolved UV-absorbing materials and of particulate chlorophyll-containing materials, both reliable indicators of the presence of surface slicks (Carlson et al., 1988). Fresh samples were collected in the morning for ship-board irradiation experiments beginning around 1000 local time. In Oregon, surface microlayer samples were collected with a glass plate (Harvey, 1966) before sunrise and then transported to Corvallis for roof-top irradiation experiments beginning around 0830 local time.

Three tracer phenols, phloroglucinol, TMP and cresol, were dissolved into distilled water and then added into microlayer samples from surface slicks and from non-slicked surfaces and into samples of subsurface waters. Final concentrations of the phenols were 5 - 10 μM for phloroglucinol, 20 μM for TMP, and 5 μM for cresol. These concentrations were similar to natural phenol concentrations (measured as phloroglucinol equivalents) in surface microlayer samples from the Gulf of Maine (Carlson and Mayer, 1980) and constituted at most a 0.009 increase in 280 nm absorbance of the seawater samples. Only phloroglucinol was used in Oregon. All three tracers were added to each California sample.

Approximately 40 ml of the seawater-phenol solutions were put in 3 cm I.D. by 28 cm long quartz tubes. The quartz tubes were then floated on the surface of incubation tanks exposed to natural sunlight. Tank temperatures were controlled at 25 °C in Oregon experiments and maintained at ambient surface temperatures (19 -24 °C) using flowing seawater in California ship-board irradiation experiments. The phenol solutions inside the tubes were at or just below the water level of the incubation tank. Dark controls consisted of quartz tubes wrapped tightly with aluminum foil, placed in the incubation tanks with the irradiated tubes. Light intensities (μEinsteins m⁻² s⁻¹) at standard PAR wavelengths (photosynthetically active radiation, 400 to 700 nm) were recorded every 20 minutes using a quantum sensor (LI-COR, LI-185A) during the irradiation experiments. We assumed that the quantum measurements were
closely related to irradiance over the full spectrum at both experimental sites because the shapes of most near-ultraviolet (greater than 310 nm) and visible spectra are nearly constant for zenith angles less than 60 degrees (Jerlov, 1976; Baker, et al., 1980). The irradiation experiments lasted about 8 hours.

At various time intervals, samples were taken from the microlayer and subsurface solutions. Degradation of tracer phenols was determined by measuring concentrations of phenols remaining in each tube. The phenols were derivatized with diazotized sulfanilic acid (DSA) to form yellow or red products in the aqueous solutions. Reaction of phenols with DSA has been used to quantify phenols in other aqueous samples (Whitlock et al., 1972; Hanson, 1973; Baiocchi et al., 1982). We modified the DSA assay to improve its sensitivity for phloroglucinol, cresol, TMP and several other phenols in seawater. Without this derivatization, phloroglucinol was difficult to extract from seawater.

DSA solution was prepared by mixing 5 ml of 55 mM sulfanilic acid (0.96 g sulfanilic acid in 100 ml distilled water) with 1 ml of dilute sulfuric acid (4.8 M). Next, 5 ml of 50 mM sodium nitrite (0.34 g sodium nitrite in 100 ml distilled water) were added slowly (over 5 minutes) into the acidic sulfanilic acid, keeping the mixture cold in an ice bath. After preparation, the DSA solution was stable for at least 4 hours if kept on ice and protected from light. DSA is fairly electrophilic, attacking ring positions para, ortho and then meta to phenolic hydroxyl groups in that order (Baiocchi et al., 1982). The coupling reaction is sensitive to pH and reaction time. The optimum pH for simultaneous quantitative determinations of these phenols in seawater was 7.5. At higher pH, multiple coupling may have occurred because multiple peaks were evident for single compounds in the HPLC chromatograms. Therefore, to derivatize the tracer phenols in seawater, 0.5 ml DSA solution was thoroughly mixed with 10 ml of the seawater, followed immediately by the slow addition of 0.22 ml of saturated NaHCO₃ solution. The reaction mixtures were then held in darkness for approximately 15 minutes. This 15 minute reaction time was required to derivatize TMP which has methyl groups at the preferred para and ortho reaction sites. The faster derivatives of phloroglucinol and cresol were stable throughout this time period. After 15 minutes, 0.3 ml of 2N HCl was added to the seawater solutions to stabilize excess DSA and the DSA-phenol derivatives long enough to remove them from aqueous solution.

The DSA-phenol derivatives were extracted from seawater using C-18 solid phase extraction columns (200 mg packing). The extracted DSA-phenol derivatives were
stable on these columns for at least one month refrigerated in the dark. Tracer phenols from 10 ml of seawater were eluted from the solid phase columns with three 0.33 ml rinses of HPLC-grade methanol, resulting in a ten-fold concentration factor. Extraction efficiency was better than 90% for phloroglucinol.

Methanol eluates from the solid phase columns were injected onto a reverse phase HPLC system. We injected 50 ml of the methanol solutions onto a 220 mm long by 4.6 mm diameter C-18 column with 5 μm packing material. The HPLC mobile phases consisted of methanol and a 10 mM NaH₂PO₄ buffer (pH = 5.5), with TBAB (tetrabutylammonium bromide, 2.5 mM) as ion pairing reagent. Gradient elution started from 75% buffer and 25% methanol and progressed in several stages to 80% methanol over 30 minutes (Fig. 2.1), followed by 100% methanol for 3 minutes to rinse the column and a 3 minute linear gradient back to 75% buffer: 25% methanol before the next injection. Flow rates were 1.5 ml min⁻¹ throughout. The DSA phenol derivatives were detected by their absorbance at 370 nm. Under these conditions, detection limits were 5 nmoles of phloroglucinol, 10 nmoles of cresol and 50 nmoles of TMP. These detection limits were quite adequate for micromolar levels of tracer phenols in 10 ml samples of seawater. For natural phenols, larger volumes of seawater can be derivatized and extracted.

2.4. RESULTS

Phloroglucinol degraded exponentially with time in all irradiated samples (e.g. Fig. 2.2). Degradation rates of phloroglucinol in microlayer samples from slicked surfaces were more rapid than in samples from corresponding subsurface waters or from non-slicked surfaces under the same natural sunlight conditions in Oregon (Fig. 2.2) and off California (Fig. 2.3). The experimental conditions for California were similar to those in Oregon except that the California incubation temperatures ranged between 20 and 25 °C and the initial phloroglucinol concentration was only 5 μM instead of 10 μM as in Oregon. Less than 10% of initial phloroglucinol disappeared in dark control samples (Fig. 2.4). Phloroglucinol degradation rates in slicked microlayers varied considerably (Table 2.1), but were always faster than degradation rates of phloroglucinol in corresponding subsurface waters. In contrast, the degradation rates in subsurface waters were similar in all experiments (Table 2.1). This pattern presumably reflects the wide range of DOM enrichment in slicks at various times and locations in contrast to the smaller range of DOM concentration in
Figure 2.1. HPLC chromatogram of 7 phenols, detected by the absorbance at 370 nm of DSA derivatives of each compound. Compounds and original concentrations in distilled water were: 1 - phloroglucinol, 0.5 µM; 2 - phenol, 0.25 µM; 3 - m-cresol, 0.5 µM; 4 - 2,6-dimethylphenol, 1.0 µM; 5 - 2,4,6-trimethylphenol, 4.0 µM; 6 - 2,4-dichlorophenol, 4.0 µM; 7 - 3,5-dibromo-4-methylphenol, 6.0 µM. The solution containing all seven phenols was concentrated 100-fold by solid phase extraction. Injection volume was 50 µl. Flow rate was 1.5 ml min⁻¹. Background line indicates mobile phase composition, progressing from 75% buffer: 25% methanol to 20% buffer: 80% methanol over 30 minutes. A 3 minute rinse in 100% methanol followed by a 3 minute linear gradient back to 75% buffer: 25% methanol occurred in the interval between successive injections.
Figure 2.2. Concentration (C) of phloroglucinol relative to initial concentration (C₀) as a function of surface irradiation in microlayer samples of a surface slick and in samples of associated subsurface seawater from Oregon, 18 July 1988. Water temperature during irradiation was 25 °C. Total time of irradiation was 7 h 25 min.
Figure 2.2.
Figure 2.3. Concentration (C) of phloroglucinol relative to initial concentration (C₀) as a function of surface irradiation in microlayer samples of slicked and non-slicked surfaces and in samples of associated subsurface seawater (subsurface) collected near San Clemente Island, CA on 25 September 1988. Water temperatures during irradiation ranged from 19 to 22 °C. Total time of irradiation was 5 h 44 min.
Figure 2.3.
Figure 2.4. Concentration (C) of phloroglucinol (filled circle from Oregon, open circle from La Jolla Bay) and m-cresol (diamond from La Jolla Bay) relative to initial concentration (C₀) without irradiation (dark controls) in microlayer samples from surface slicks.
Figure 2.4.
Table 2.1. First order degradation rate constants for phloroglucinol and half-lives (in mid-day hours) for phloroglucinol and TMP in microlayer samples from slicked and non-slicked surfaces and in subsurface samples from Oregon (July) and California (September). Surface and subsurface samples received identical irradiation. TMP half-lives were calculated using linear slopes extrapolated between initial and final concentrations.

<table>
<thead>
<tr>
<th>Date</th>
<th>Phloroglucinol Rate Constants (m² Einstein⁻¹)</th>
<th>Phloroglucinol Half-lives (hrs)</th>
<th>TMP Half-lives (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SFC  BW</td>
<td>SFC  BW</td>
<td>SFC  BW</td>
</tr>
<tr>
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<td>0.660 0.050</td>
<td>0.15 1.93</td>
<td>- -</td>
</tr>
<tr>
<td>9/15/88</td>
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<td>- -</td>
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<tr>
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<td>0.042 0.022</td>
<td>2.28 3.15</td>
<td>3.6 -</td>
</tr>
<tr>
<td>9/22/88</td>
<td>0.045 0.030</td>
<td>2.13 3.21</td>
<td>1.8 -</td>
</tr>
<tr>
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<td>1.92 2.75</td>
<td>3.4 3.6</td>
</tr>
<tr>
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<td>- 2.75</td>
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</tr>
<tr>
<td>9/25/88</td>
<td>0.120 0.041</td>
<td>0.80 2.35</td>
<td>1.7 3.1</td>
</tr>
</tbody>
</table>
non-slicked microlayers or in subsurface waters (Carlson, 1982b). With one exception, the ratios of microlayer phloroglucinol degradation to subsurface degradation varied directly with the ratios of microlayer to subsurface UV absorbance in those samples in which both photodegradation and absorbance were measured (Fig. 2.5).

Photo-induced degradation of TMP was generally slower than phloroglucinol degradation in slicked microlayer samples and in subsurface samples, even though both compounds were exposed in the same samples to the same irradiation (Table 2.1). TMP concentrations in some irradiated subsurface and microlayer samples and in some dark controls varied during the first two hours of incubation, first apparently disappearing and then re-appearing. This variability, which may have been due to rapid adsorption of the relatively insoluble TMP onto container surfaces followed by slow desorption, prevented calculation of exponential decay constants. In general, however, TMP degradation was greater in slick samples than in subsurface samples (Table 2.1).

Degradation rates of cresol were lower than those of phloroglucinol or TMP at the same sunlight conditions. The maximum cresol degradation (50% of the initial 5 μM concentration) occurred in a sample from a surface slick collected on 25 September - that sample also had maximum degradation of phloroglucinol and TMP among California samples and high UV absorbance enrichment. Cresol also degraded in a sample collected on 22 September. Cresol concentrations in both these samples declined slightly during the first two hours and then increased before their final decline. The initial concentration decreases were presumably due to adsorption effects similar to those postulated for TMP. Cresol degradation in three other California microlayer samples was less than 20%. Cresol degradation in subsurface water samples was always less than 20%.

In order to identify mechanisms of photo-induced degradations of phloroglucinol and other phenols, we added a singlet oxygen quencher, sodium azide (NaN₃, final concentration = 50 μM), into some samples from slicked microlayers. The degradation rate of phloroglucinol in the presence of sodium azide was approximately 25% slower than degradation without azide in the sample of 25 September, with azide inhibition evident during the first three hours of exposure (Fig. 2.6). After longer exposures phloroglucinol concentrations had dropped to near detection limits and azide effects were no longer evident; azide itself is photo-sensitive and it may also have degraded. Azide effects were not evident for TMP or cresol in this sample.
Figure 2.5. Ratios of first-order rate constants for photodegradation of phloroglucinol in surface microlayer samples relative to associated subsurface samples compared with surface to subsurface ratios (enrichments) of UV absorbance (280 nm) in the same samples. All samples from near San Clemente Island, California, except for the outlying value with a high UV absorbance ratio which was collected in La Jolla Bay. Data from slicked and non-slicked surfaces.
Figure 2.5.
In a sample exposed on 21 September degradation of TMP was slower when azide was present (Fig. 2.6). Because cresol did not usually degrade, azide effects on cresol degradation were not evident.

We calculated half-lives of phloroglucinol and TMP, assuming first-order reaction kinetics, for each microlayer sample from a surface slick. We estimated an average summer mid-day sunlight intensity of 2000 μEinsteins m⁻² s⁻¹ (1000 watts m⁻²) at PAR wavelengths to convert rates measured as a function of irradiation into half-lives in terms of mid-day hours for phloroglucinol and TMP. Phloroglucinol half-lives calculated in this way ranged from 0.15 to 2.3 hours for surface microlayers, with the shortest half-life in an Oregon experiment in which incubation temperature was 25 °C. Half-lives for phloroglucinol in subsurface waters at surface light intensities were 1.9 to 3.2 hours, with the shortest half-life again from the warmer Oregon experiment. Microlayer phloroglucinol half-lives were always shorter than subsurface half-lives. TMP half-lives in microlayer samples (1.7 to 3.6 hours) were also shorter than subsurface half-lives (3.6 to 6.0 hours).

2.5. Discussion

We equate disappearance of tracer phenols with degradation, although we do not yet know the degradation products. It is clear that phenol degradations we observed were photochemical rather than microbial: degradation in the absence of light was never more than 10% of the degradation observed in light. Microbiological consumption can affect surface microlayer components such as amino acids (Carlucci et al., 1985), but those compounds are preferred heterotrophic substrates and not photochemically reactive. Hwang et al. (1986) reported that microbial degradation rates of mono-chlorinated phenols and of phenol itself were faster than photodegradation rates of the same compounds in estuarine waters, but that photodegradation of poly-chlorinated phenols exceeded microbial degradation. When microbial degradation rates in that work were significant, as in the case of phenol, total degradation rates were still slow, with half-lives on the order of 30 days. Slow rates such as those would not have affected degradation in our experiments.

We are not aware of comparable rates for phloroglucinol photodegradation in other natural waters or laboratory solutions, but investigations have been made of photodegradation of TMP and cresol. Faust and Hoigne (1987) found half-lives of 4.3 and 24 hours for TMP and cresol, respectively, at light exposures equivalent to
Figure 2.6. Concentration (C) of phloroglucinol (upper) and TMP (lower) relative to initial concentrations ($C_0$) as a function of surface irradiation in samples of slicked surface microlayers with and without 50 mM NaN$_3$. Samples from California, collected in La Jolla Bay on 21 September (TMP) and near San Clemente Island on 25 September (phloroglucinol).
Figure 2.6.
June surface irradiation in laboratory solutions containing 4.1 mg carbon l\(^{-1}\) of fulvic acid. That TMP half-life is consistent with half-lives we observed in samples of subsurface seawater under surface irradiation (TMP half-lives 3.6 to 6.0 h) but longer than half-lives we observed in microlayer samples. The relative reaction rates of TMP and cresol observed by Faust and Hoigne are also consistent with our observations that cresol photodegradation was much slower than that of TMP. Scully and Hoigne (1987) also estimated very long half-lives (> 100 h) for photo-induced degradation of another cresol, p-cresol (4-methyl phenol) at the pH of natural waters. Some polychlorinated phenols have much shorter residence times: Hwang et al. (1986) estimated half-lives of 0.6 to 3.0 hours for polychlorinated monophenols in surface estuarine waters. It appears, therefore, that the half-lives we observed for phloroglucinol and TMP in subsurface waters are consistent with photodegradation rates of these and other phenols in other natural surface waters. The half-lives we observed in microlayer samples from surface slicks, however, seem much shorter than phenol half-lives in most other aquatic systems. Other microlayer components of surface slicks, including perhaps pollutants, may be subject to or participants in similar rapid photochemical alteration.

In most of our samples, phenol photodegradation rates were correlated with UV absorbance enrichments. This correlation may have been coincidental: photodegradation and UV absorbance enrichment may have been independently related to the presence of slicks and associated dissolved organic materials but not necessarily related to each other. Or, the correlation may indicate that UV absorbance of a surface sample is related to, perhaps causal to, the photo-reactive properties of surface slick materials. Such a relation might be expected because UV-absorbing materials are by definition potential photoreactants and because known photoreactants such as humic and fulvic acids (e.g. Haag et al., 1984b; Faust and Hoigne, 1987) absorb light at UV wavelengths. It is also possible that some UV-absorbing materials in surface microlayers are photochemically inert and therefore decrease the effective exposure of other surface and near-surface materials. Our sample of 22 September, which had a surface-to-subsurface absorbance ratio of 4.7 but a photodegradation rate constant ratio of only 1.47 may be an example of such effects, perhaps due to shading, scavenging, or quenching.

If the relation between phenol photodegradation and microlayer UV absorbance observed for these few samples can be extended to a larger number of samples, it may be possible to predict photochemical effects based on UV absorbance measured in
surface microlayers. If, for example, average microlayer UV absorbance enrichment for a region is 2.0, then the ratio of microlayer to subsurface photodegradation rate constants for phloroglucinol, obtained from Figure 5, will be 2.4. Using the average subsurface rate constant measured here of 0.036 m² Einstein⁻¹ and a surface \( C_0 \) of 5 \( \mu \text{M} \) (Carlson and Mayer, 1980), the surface phloroglucinol degradation rate over the region will be 4.3 \( \mu \text{M} \text{ m}^{-2} \text{ day}^{-1} \). If \( C_0 \) is equal to a steady state concentration, then inputs must balance outputs and the input rate must also be 4.3 \( \mu \text{M} \text{ m}^{-2} \text{ day}^{-1} \). For subsurface concentrations of 1 mM (Carlson and Mayer, 1980), at least four volumes of subsurface water must exchange with microlayer water each daylight period to maintain the surface phenol concentrations. In intense slicks with UV absorbance enrichment factors of five or greater (Carlson, 1982b; 1983) photochemical degradation of compounds such as phloroglucinol may be very rapid. If measurements show phloroglucinol-type molecules to be present in those slicks during daylight hours, then the processes which supply those molecules to the slick must also be very active. If the putative microlayer photoreactants become unreactive or are otherwise altered or consumed, then they also must be resupplied. At present these calculations are unreliable because we do not know the generality of the relation of photochemical reaction to surface UV absorbance, but they do suggest that one could estimate input rates to the surface microlayer and microlayer residence times of individual phenols (or other molecules of equivalent size) if one knew surface and subsurface concentrations of the natural phenol, average photodegradation rates of that phenol in subsurface water, and the average surface UV absorbance. It is also possible that microlayer photodegradations of other molecules (e.g. flavins) or of other chemical properties (e.g. fluorescence) are correlated with microlayer UV absorbance and can be predicted from its measurement.

We do not yet know the mechanism(s) by which the tracer phenols degrade, or the products of the degradation. Although phloroglucinol and the other phenols might undergo direct photolysis, it is also likely that enhanced photodegradation in surface microlayer samples was due to photo-induced reactions. Several photochemically-reactive species are produced when water containing natural dissolved organic materials is exposed to sunlight. Of those, singlet oxygen and peroxides have been shown to induce the degradation of phenolic materials (Faust and Hoigne, 1987; Scully and Hoigne, 1987). Phenol degradations as a result of photo-induced production of singlet oxygen proceed at rates directly related to the dissociation
of phenolic hydroxyl groups to phenoxides (Scully and Hoigne, 1987). In our data, phloroglucinol, with lowest $pK_a$ of the three tracers, was more reactive at seawater pH than TMP or cresol, and the addition of NaN$_3$, which quenches singlet oxygen, did slow the degradations of phloroglucinol and TMP, albeit only slightly. However, our observations that cresol was less reactive than TMP despite its lower $pK_a$ were not consistent with degradation involving singlet oxygen. The relative rates of TMP and cresol degradation were more consistent with patterns observed for phenol degradation due to photo-induced production of peroxides (Faust and Hoigne, 1987). Thus our data do not definitively indicate or preclude mechanisms involving singlet oxygen or peroxides, and it may be that both of those and other mechanisms were involved.

Whatever the mechanisms, the products of phenol photodegradation were presumably oxidized relative to the reactants. Perbet et al. (1982) suggested that photodegradation of phloroglucinol involved oxidized intermediate products such as quinones, but were unable to recover those unstable materials. In surface microlayers, quinones would be more soluble than their less-oxidized precursors with less tendency to remain at or near the surface. Quinones might also polymerize and thereby alter the molecular weight of the microlayer organic materials and perhaps the rheological properties of the microlayer itself (Carlson, 1989). Photodegradation products of molecules like cresol or TMP might be similar to those from phloroglucinol; they are likewise unknown. Several studies have shown the production of low molecular weight carbon compounds (e.g., carbon monoxide, carbonyls) from irradiated seawater (Conrad and Seiler, 1980; Redden, 1982; Mopper and Stahovec, 1986). It is not known whether or by what mechanism phenols might be a source of those products.

2.6. **Summary**

Although the mechanisms and products remain unknown, it is clear from this work that oceanic surface microlayers can be sites of very active photochemistry. In surface slicks especially, microlayer photochemistry will be considerably underestimated by simply extrapolating near-surface rates to surface light intensities. Enhanced photodegradation in surface slicks may be due to increased abundance of photoreactants related to the UV absorbance properties of organic materials in the slicks, to altered configurations of those molecules because they are near the
interface, or to the presence of reactive or catalytic components from the atmosphere. Surface microlayers, and again, surface microlayers from surface slicks especially, may therefore represent regions in which photochemical alterations of oceanic dissolved organic material are highly effective and perhaps unique. Understanding rates of surface photochemical alteration may allow determination of surface residence times of photoreactive molecules and of exchange rates between surface microlayers and underlying waters.

ACKNOWLEDGEMENTS

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3. THE ROLE OF PHOTO-INDUCED SINGLET OXYGEN IN
TRANSFORMATIONS OF PHENOLIC COMPOUNDS IN SEA SURFACE
MICROLAYER SAMPLES

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(In Preparation for Marine Chemistry)
3.1. ABSTRACT

Addition of pterin as a photosensitizer into surface microlayer samples from surface slicks accelerated the sunlight-induced transformations of phenolic compounds added to those samples. Faster transformation rates observed in unaltered slick samples than in subsurface bulkwaters under the same light intensities were therefore ascribed to higher concentrations of natural photosensitizers in the slicks. Transformation rates of phenolic compounds were significantly inhibited by addition of a singlet oxygen (\(^{1}\text{O}_2\)) quencher and by removal of oxygen from samples regardless of photosensitizer concentrations. These observations indicate that triplet states of photosensitizers such as pterin transfer energy primarily to oxygen molecules in surface seawater to form \(^{1}\text{O}_2\). Oxidation of phenols by photo-produced \(^{1}\text{O}_2\) seemed to be the major pathway for transformation of phenolic compounds in seawater - other photo-produced reactive transients (e.g. organic peroxy radicals) seemed much less important. Measured rate constants between tracer phenols and \(^{1}\text{O}_2\) were consistent with those in freshwaters.
3.2. **INTRODUCTION**

Natural phenolic compounds and other ultraviolet-absorbing materials have been used as indicators of marine surface microlayer chemical enrichments (Carlson, 1982b; Carlson et al., 1988; Moum et al., 1990) and rheological properties (Carlson, 1987). However, some of the phenolic compounds may undergo sunlight-induced transformations while in surface microlayers (Lin and Carlson, 1991). Although rates of these photo-transformations have been estimated, additional knowledge about these photo-processes and photo-transformation mechanisms is needed to understand the origin, persistence and fate of phenolic and other photo-sensitive compounds in marine surface microlayers. Because photo-transformations of organic materials anywhere in sun-lit seawater are poorly known, accurate descriptions of rates and mechanisms of phenol photo-transformations in surface microlayers may provide information about photo-transformations of other materials and assessment of possible photo-degradation pathways for organic pollutants in seawater.

Natural dissolved organic matter (DOM) has been recognized as a potential source of photo-produced reactive transients when exposed to natural solar radiation in surface seawater. One reactive transient of environmental interest is photo-produced singlet oxygen ($^1\text{O}_2$), formed by energy transfer from photosensitizer triplet states to dissolved oxygen in natural waters, usually referred to as Type 2 photosensitization (Wolff et al., 1981; Haag et al., 1984a). Type 2 photosensitization processes to generate $^1\text{O}_2$ have been observed in freshwaters (Zepp et al., 1981; Haag and Hoigne, 1986) and in seawater (Momzikoff et al., 1983b). In addition to humic-like substances, many fluorescent nitrogen-containing heterocyclic compounds may serve as natural photosensitizers in seawater, especially including pteridines (Landymore and Antia, 1978; Chahidi et al., 1981; Momzikoff et al., 1983a) and flavins (Joussot-Dubien and Kadiri, 1970; Momzikoff et al., 1983b; Mopper and Zika, 1987). Due to their strong absorbance of sunlight (Chahidi et al., 1981) and their high efficiency for intersystem crossing from singlet to triplet states (Heelis, 1982), these and other sunlight absorbing compounds with triplet state energy greater than 22.5 Kcal / mol can transfer their energy to dissolved oxygen to generate $^1\text{O}_2$ and thereby promote photochemical reactions with organic compounds in the sea. However, deactivation of $^1\text{O}_2$ can also take place in seawater, primarily due to physical quenching of $^1\text{O}_2$ by water molecules. Organic compounds, such as phenols, can also quench photo-produced $^1\text{O}_2$ (Foote, 1979), but these organic quenching processes are usually
neglected unless very high concentrations of organic compounds are present, as in highly polluted environments (Zafiriou et al., 1984). Likely schemes for generation of $^{1}\text{O}_2$, deactivation, and reactions with organic materials are summarized in the following equations:

\[
\begin{align*}
\text{oPS (photosensitizers)} \xrightarrow{\text{hv}} & \text{1PS} \xrightarrow{-} \text{3PS} \\
\text{3PS} \xrightarrow{-} & \text{oPS + Heat} \\
\text{3PS + O}_2 \xrightarrow{-} & \text{1O}_2 + \text{oPS (Energy Transfer)} \\
\text{1O}_2 + \text{H}_2\text{O} \xrightarrow{-} & \text{O}_2 + \text{H}_2\text{O (Physical Quenching)} \\
\text{1O}_2 + \text{Organic Quencher} \xrightarrow{-} & \text{O}_2 + \text{Q (Physical Quenching)} \\
\text{1O}_2 + \text{Organics} \xrightarrow{-} & \text{Transformation Products}
\end{align*}
\]

The life-time of $^{1}\text{O}_2$ in most aqueous solutions is as short as 2-4 microseconds (Merkel and Kearns, 1972; Scully and Hoigne, 1987), but this is still sufficient for reaction with organic compounds. The simultaneous generation and deactivation of $^{1}\text{O}_2$ leads to a steady-state concentration of $^{1}\text{O}_2$. These steady-state concentrations of $^{1}\text{O}_2$, $[^{1}\text{O}_2]_{ss}$, vary by several orders of magnitudes in various water types under similar solar irradiation conditions (Haag and Hoigne, 1986). The main factors affecting $[^{1}\text{O}_2]_{ss}$ appear to be natural photosensitizer concentrations and the absorption rates of incident light in surface water (Haag and Mill, 1989). In surface seawater, $[^{1}\text{O}_2]_{ss}$ was reported to be $2 \times 10^{-14}$ M under solar irradiation, a value lower than in organic-rich freshwaters under similar solar irradiation (Haag and Hoigne, 1986). However, a higher value of $[^{1}\text{O}_2]_{ss}$ might be expected in marine surface microlayers where the maximum sunlight radiation is received and where potential natural photosensitizers may accumulate relative to subsurface waters.

The objectives of this study were to determine by the use $^{1}\text{O}_2$ inducers and quenchers the role of $^{1}\text{O}_2$ in phenol photo-transformations in surface seawater and to determine whether heterocyclic materials such as pteridines might sensitize such transformations. Previous work has suggested the importance of $^{1}\text{O}_2$ in phenol oxidation and transformations in freshwater (Scully and Hoigne, 1987) and in seawater (Lin and Carlson, 1991), but there has been little supporting evidence and connection of those processes to the presence or photosensitizing properties of fluorescent materials such as the pteridines. We also explored the use in seawater of a nitroxide trap as a probe for photo-transformations involving an additional class of photo-induced reactive transients, carbon-centered radicals.
3.3. MATERIALS AND METHODS

3.3.1. Samples and Chemicals

Microlayer samples from surface slicks (SFC) and bulkwater samples from 15 cm below the surface (BW) were collected with an automated surface microlayer sampler (Carlson et al., 1988) deployed from R/V Wecoma during the SLIX89 experiment off the southern California coast. These samples were used immediately after collection for real-time experiments. Portions were stored for 6 months in the dark at 0-4 °C for later laboratory experiments.

Analytical grade phloroglucinol (PGL) and 1,4-diazabicyclo [2,2,2] octane (DABCO) were obtained from Fluka, analytical grade 2,3-dimethylphenol (2,3-DMP), 2,3,5-trimethylphenol (2,3,5-TMP) and pterin were obtained from Sigma, and 3-aminomethyl-2,2,5,5,-tetramethyl-1-pyrrolidinyloxy (3-AMP) was obtained from Aldrich. All chemicals were used as received. Stock solutions of the phenols, of DABCO and of pterin were prepared in distilled deionized water (Millipore-Q system) and stored in the dark at 0-4 °C. 3-AMP was dissolved in sodium borate buffer (pH 8.2) and stored at 0-4 °C. Prior to an irradiation experiment, appropriate amounts of the phenol stock solutions were added into the SFC and BW samples. Pterin, DABCO and 3-AMP were added in diagnostic tests. In same cases, reduced oxygen conditions were obtained by purging seawater samples in incubation tubes with N₂ for 15 minutes before irradiation. Re-adjustment of seawater pH, altered by addition of DABCO, was performed by adding appropriate amounts of 2N HCl to the samples.

3.3.2. Irradiation Experiment

Irradiation experiments under natural sunlight were undertaken on R/V Wecoma. Equipment for the irradiation experiments has been described previously (Lin and Carlson, 1991). Dark controls were performed with incubation tubes completely wrapped by aluminium foil incubated simultaneously with irradiated samples. In laboratory experiments, an ultraviolet light reactor with a Hanovia 679A36 Medium Pressure Mercury Lamp (450 W, maximum emissions at 320 and 360 nm) was employed. A water jacket was used to keep the reactor in a range of 20-25 °C. Pyrex glass test tubes used for laboratory incubations were placed parallel to the lamp at
distances of 15 cm for irradiation. The combination of Pyrex transmittance characteristics and Hanovia emission spectra provided ultraviolet irradiation around 360 nm (near-ultraviolet). At intervals of 5-15 minutes of irradiation, samples were removed to determine concentrations of the phenols. Disappearance of the phenols ([phenols]/[phenols]₀) during irradiation by sunlight or the Hanovia lamp was assumed to be due to photo-induced transformations. Quantitative analyses of phenol concentrations were performed by reverse phase HPLC with a C_{18} column and 370 nm UV detector following coupling reaction between phenols and diazoitized sulfanilic acid (DSA) directly in seawater and solid phase extraction of the diazoitized phenols from seawater. Details of the coupling reaction and HPLC procedures have been published (Lin and Carlson, 1991).

3.4. Results

3.4.1. Ship-board Natural Sunlight Experiments

Transformation (disappearance) of phloroglucinol (PGL, 5 μM) after irradiation in sunlight (1000 W m⁻²) in marine surface microlayer (SFC) and subsurface bulkwater (BW) samples is demonstrated in Fig. 3.1. Transformation of PGL in distilled deionized water and in SFC sample with addition of pterin (5.0 μg/l) are also shown (Fig. 3.1). The transformations of PGL under natural sunlight in all seawater samples took an approximately first-order form with respect to the concentration of PGL. Experimental first-order rate constants of PGL transformation in different samples were calculated and are listed in Table 3.1. Transformation rate of PGL in SFC sample was 1.45 times faster than in the BW sample under the same light (Fig. 3.1). With addition of pterin, PGL disappeared completely after less than 2 hours of sunlight. The pterin-assisted rate constant was about eight-fold greater than in the SFC sample without pterin. On the other hand, disappearance of PGL in distilled deionized water was less than 20% after six hours of roof top sunlight in Corvallis, OR. PGL disappearance in the dark even with pterin addition was also less than 20% after 8 hours of incubation (Fig. 3.1). Rate constants for PGL transformation in distilled deionized water and in the dark with pterin were less than 6% of total k_{exp} in SFC and less than 1% of total k_{exp} in SFC with addition of pterin (Table 3.1).
Figure 3.1. \( [PGL]/[PGL]_0 \) versus total exposure time to sunlight in southern California (October, 1989) in slicked surface microlayer (SFC) sample (open square), subsurface bulk seawater (SBW) sample (solid square) and SFC sample with addition of pterin (5 \( \mu \)g liter\(^{-1}\)) as a photosensitizer (open diamond). All the lines are first-order fit. Dark control of SFC sample (solid diamond) with addition of pterin started simultaneously with other samples in the absence of sunlight. Irradiation of PGL in distilled water (solid circle) was performed under Oregon sunlight (Aug, 1989). All initial concentrations of PGL were 5 \( \mu \)M.
Figure 3.1.

PHLOROGLUCINOL
SUNLIGHT EXPOSURE

[Diagram showing a graph with time (min) on the x-axis and \([\text{PGL}] / [\text{PGL}]_0\) on the y-axis, depicting the decay of phloroglucinol over time.]

Figure 3.1.
Table 3.1. Experimental first-order rate constants ($k_{exp}$) of PGL in seawater samples collected in southern California (October, 1989) and in distilled water. Sunlight intensity was assumed as an average of 1000 W m$^{-2}$.

<table>
<thead>
<tr>
<th>Samples/Addition</th>
<th>Rate Constants (min$^{-1} \times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Microlayer Sample (SFC)</td>
<td>6.7</td>
</tr>
<tr>
<td>Subsurface Bulk Seawater (SBW)</td>
<td>4.7</td>
</tr>
<tr>
<td>SFC with Pterin (5 µg/l)</td>
<td>54</td>
</tr>
<tr>
<td>SFC with Pterin in the Dark</td>
<td>0.49</td>
</tr>
<tr>
<td>Distilled Water (Mil-Q)</td>
<td>0.39</td>
</tr>
</tbody>
</table>
3.4.2. Laboratory Irradiations

Under near-ultraviolet light from the Hanovia lamp, approximately 70% PGL disappeared after 45 minutes irradiation of the stored SFC sample (Fig. 3.2a). With addition of 2.5 μg/l of pterin, PGL disappeared completely after 15 minutes of irradiation in the same sample. Similar to transformation kinetics in sunlight, transformations of PGL under near-ultraviolet radiation were approximately first-order with respect to PGL (Fig. 3.2a), but the rates were more rapid (Table 3.2). Transformation rates of two other phenolic compounds, 2,3-dimethylphenol (2,3-DMP, 30 μM) and 2,3,5-trimethylphenol (2,3,5-TMP, 30 μM), were slower than those for PGL. 2,3,5-TMP disappeared faster than 2,3-DMP under the same light conditions (Figs. 3.2b and 3.2c). Experimental transformation rate constants for all three phenols estimated based on the first-order reactions are listed in Table 3.2. With addition of pterin, transformation rates of 2,3-DMP and 2,3,5-TMP were also accelerated, though the relative reactivity of the three phenols remained in the same order (Table 3.2). Fig. 3.3 shows the linear correlation (R² = 0.94) between PGL (%) remaining in solution after 2.5 minutes of irradiation and concentration of pterin, demonstrating that transformation rates of PGL, and perhaps of all three phenols, were proportional to the amounts of pterin added. When oxygen was removed (by N₂ purging), transformation rates of PGL were reduced by 60 % in comparison with PGL in oxygen-saturated SFC sample at the same light irradiance (Fig. 3.4). With reduced oxygen in SFC samples, addition of pterin did not effectively increase transformation rates of PGL (Fig. 3.4).

The involvement of photo-produced singlet oxygen (¹O₂) in phenol transformations was indicated by reductions in the transformation rates following addition of 1,4-diazabicyclo [2,2,2] octane (DABCO) as a ¹O₂ quencher (Fig. 3.2). The first-order apparent rate constant for PGL transformation in a SFC sample supplemented with DABCO (1 mM) was reduced by a factor of more than six in comparison with the rate constant without DABCO. DABCO only partially inhibited PGL transformation, however, because there was still a disappearance of PGL (40%) in 40 minutes of irradiation (Fig. 3.2a). First-order transformations of 2,3-DMP and 2,3,5-TMP seemed to be completely stopped by addition of 1 mM DABCO (Figs. 3.2b and 3.2c). Figure 3.5 demonstrates the inhibiting effect of DABCO at various concentrations on transformations of the phenols. It appeared that changes in concentration of DABCO did not affect inhibition for PGL or the other two phenols.
Figure 3.2.

(a) $[\text{PGL}]/[\text{PGL}]_0$ versus total exposure time to 450 Watt Hanovia lamp in SFC sample (open circle), SFC sample with addition of 2.5 µg liter$^{-1}$ pterin (open diamond), and SFC sample with addition of 1 mM DABCO (solid circle). Initial concentrations of PGL were 5 µM.

(b) $[\text{DMP}]/[\text{DMP}]_0$ versus total exposure time to 450 Watt Hanovia lamp in SFC sample (open circle), SFC sample with addition of 2.5 µg liter$^{-1}$ pterin (open diamond), and SFC sample with addition of 1 mM DABCO (solid circle). Initial concentrations of DMP were 30 µM.

(c) $[\text{TMP}]/[\text{TMP}]_0$ versus total exposure time to 450 Watt Hanovia lamp in SFC sample (open circle), SFC sample with addition of 2.5 µg liter$^{-1}$ pterin (open diamond), and SFC sample with addition of 1 mM DABCO (solid circle). Initial concentrations of TMP = 30 µM.
PHLOROGLUCINOL
UV LAMP EXPOSURE

Figure 3.2(a).
Figure 3.2(b).
Figure 3.2(c).
Table 3.2. Transformation rate constants and relative reactivities of phenols in SFC sample under irradiation from Hanovia lamp, and estimated second-order rate constants ($k_r$) with respect to $^1O_2$ on the basis of a sunlight-produced $[^1O_2]_{ss}$ value ($2\times10^{-14}$ M) in surface seawater (Haag and Hoigne, 1986). Relative reactivity calculated by using PGL rate constant in unaltered SFC as reference.

<table>
<thead>
<tr>
<th>Phenols</th>
<th>$k_{\text{exp}}$ (min$^{-1}$)</th>
<th>$k_{\text{exp}}$ (pterin) (min$^{-1}$)</th>
<th>Reactivity</th>
<th>$k_r$ (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGL</td>
<td>0.074</td>
<td>0.23</td>
<td>1</td>
<td>$8.0\times10^7$</td>
</tr>
<tr>
<td>2,3-DMP</td>
<td>0.0082</td>
<td>0.048</td>
<td>0.11</td>
<td>$9.0\times10^6$</td>
</tr>
<tr>
<td>2,3,5-TMP</td>
<td>0.032</td>
<td>0.092</td>
<td>0.43</td>
<td>$3.5\times10^7$</td>
</tr>
</tbody>
</table>
Figure 3.3. Correlation between \([PGL]/[PGL]_0\) at 2.5 minutes of UV irradiation from 450 Watt Hanovia lamp in SFC samples and concentrations of pterin added as a photosensitizer \((R^2 = 0.94)\).
Figure 3.3.

\[ Y = -0.06 \times X + 0.78 \]

\[ R^2 = 0.94 \]
Figure 3.4. $[\text{PGL}] / [\text{PGL}]_0$ versus total exposure time to 450 Watt Hanovia lamp in SFC sample (open circle), de-oxygenated SFC sample (solid circle) and de-oxygenated SFC sample with addition of 2.5 $\mu$g liter$^{-1}$ pterin as a photosensitizer (open diamond). Removal of oxygen from samples was performed by purging samples with $N_2$ for 10-15 minutes.
Figure 3.4.
Figure 3.5. $[\text{PGL}]/[\text{PGL}]_0$ (open circle), $[\text{DMP}]/[\text{DMP}]_0$ (open triangle) and $[\text{TMP}]/[\text{TMP}]_0$ (open diamond) at 40 minutes of irradiation from Hanovia lamp in SFC sample with addition of various amounts of DABCO.
Figure 3.5.
In other words, 1mM DABCO was sufficient to reduce photo-produced $^1\text{O}_2$ in the slicked microlayer samples and to halt transformations via $^1\text{O}_2$ mechanisms. When DABCO (1mM) and pterin (2.5 $\mu$g/l) were added together (Fig. 3.6), it appeared that 1 mM DABCO had sufficient quenching capability to deactivate any $^1\text{O}_2$ generated by pterin under these light conditions.

The effect of 3-aminomethyl-2,2,5,5,-tetramethyl-1-pyrrolidinyloxy (3-AMP) addition, an effective transient radical trapping reagent, on the transformation of PGL was not as expected (Fig. 3.7). Instead of suppressing transformations of PGL in the SFC sample, the nitroxide increased transformations of PGL by amounts proportional to the nitroxide concentrations.

Assuming that $^1\text{O}_2$ was the predominant reactant in transformation of the phenolic tracers, we established an expression for the reactions of sunlight-generated $^1\text{O}_2$ with phenols in seawater as follows:

$$-d[\text{phenols}] / dt = k_r [^1\text{O}_2]_{ss} [\text{phenols}] \quad (3.6)$$

where $k_r$ denotes the second-order reaction rate constant with respect to $[^1\text{O}_2]_{ss}$ and phenol concentrations in seawater and the measured experimental first-order rate constants given in Table 3.1 are in fact pseudo-first-order kinetics with steady-state concentrations of $^1\text{O}_2$, $[^1\text{O}_2]_{ss}$ (e.g., the pseudofirst-order rate constants ($k_{exp}$) are equal to the product of $k_r$ and $[^1\text{O}_2]_{ss}$). Then, $k_r$ was calculated for each of the three tracers by Eqn. 3.7:

$$k_r = k_{exp} / [^1\text{O}_2]_{ss} \quad (3.7)$$

for a particular value of $[^1\text{O}_2]_{ss}$. Setting $[^1\text{O}_2]_{ss} = 2 \times 10^{-14}$ M (Haag and Hoigne, 1986) we estimated $k_r$ for PGL with $^1\text{O}_2$ (Table 3.2). Using the reactivities of 2,3-DMP and 2,3,5-TMP relative to PGL under the UV lamp (Table 3.2), the $k_r$'s for 2,3-DMP and 2,3,5-TMP with $^1\text{O}_2$ were also estimated (Table 3.2).

3.5. DISCUSSION

3.5.1. Photosensitization in Seawater

Because the maximum absorption of light by PGL occurs at 270 nm (Scott, 1964), direct photolysis of PGL or other photo-transformations of PGL in seawater as a
Figure 3.6. $[\text{PGL}] / [\text{PGL}]_0$ versus total exposure time to 450 Watt Hanovia lamp in SFC sample (open circle), SFC sample with addition 2.5 $\mu$g liter$^{-1}$ pterin (open triangle), and SFC sample with addition of 2.5 $\mu$g liter$^{-1}$ pterin and 1mM DABCO (solid circle).
Figure 3.6.
Figure 3.7. \([PGL]/[PGL]_0\) versus total exposure time to 450 Watt Hanovia lamp in de-oxygenated SFC sample (open circle) and de-oxygenated SFC sample with addition of 43.5 \(\mu\text{M}\) 3-AMP (solid square) and 87.0 \(\mu\text{M}\) 3-AMP (solid circle). The samples were purged with \(\text{N}_2\) for 10-15 minutes.
Figure 3.7.

PHLOROGLUCINOL + AMP
UNDER O2 REDUCED CONDITION

$\frac{[PGL]}{[PGL]_0}$ vs TIME (min)
consequence of absorbing short wavelength sunlight is unlikely. The low transformation rates of PGL in pure water without photosensitizers (only 6% of rates in seawater) confirm this assumption - direct photo-reaction with sunlight is probably not an important reaction pathway for phenolic compounds in seawater. Faust and Hoigne (1987) reached a similar conclusion about alkylphenols in freshwater. There were also no significant changes in PGL concentrations in samples incubated with pterin but without light. It seems clear, therefore, that phenol photo-transformations in seawater are secondary photo-reactions that rely on photosensitizers and probably on photo-produced reactive transients.

The addition of a known photosensitizer such as pterin greatly accelerated PGL transformation rate in SFC samples. Absorption of near-ultraviolet wavelengths of sunlight by nitrogen-containing heterocyclic compounds such as pteridines (Momzikoff, 1983b; Zika, 1981) may result in Type 2 photosensitization: an excited singlet may undergo intersystem crossing to a triplet state and transfer energy to dissolved oxygen in seawater to produce singlet oxygen ($^{1}$O$_{2}$) (Landymore and Antia, 1978; Chahidi et al., 1981). The effect of pterin on transformation of PGL and of di- and trimethylphenols is probably strong evidence for photosensitized pathways in general in seawater. Oxygen is the predominant acceptor for energy transferred from photosensitizer triplets in surface seawater, so $^{1}$O$_{2}$ is implicated as an important intermediate in these photosensitized transformations.

Photosensitized transformations of phenols are thus influenced by environmental and chemical factors. Environmental factors include abundance or supply rate of photosensitizers, wavelengths of light available for excitation (essentially, depth and water transparency, neither of which is very important in surface microlayers), and abundance of oxygen to serve as an energy acceptor. In our experiments abundance of pterin strongly influenced phototransformation of PGL and other phenols. There were also hints of wavelength affects. Phototransformation of PGL induced by the near-ultraviolet radiation of Hanovia lamp was faster than in any sample under sunlight even though lower concentrations of pterin were present and the samples were several months old. These faster transformations may have been due to greater overall intensities from the UV lamp, or they may reflect higher production rates of $^{1}$O$_{2}$ at intense near-ultraviolet frequencies of the lamp compared with less intense shortwave radiation in sunlight (Haag et al., 1984b). In work not reported here, PGL transformation in sunlight was greater in quartz tubes than in polycarbonate bottles (Lin and Carlson, in prep.), further indication of the importance of short wavelengths
for photosensitized phototransformations. Oxygen was also an important environmental factor: when oxygen was removed from our solutions, phototransformations were greatly reduced even when additional photosensitizers were added. It is likely that the abundance and absorption properties of photosensitizers and, to a lesser extent, the availability of oxygen, all of which were determining factors in our tracer experiments, are determining factors for most photochemical reactions in seawater.

Chemical properties of the molecules being transformed and light absorption properties and the wavelength-dependent quantum yields and energy levels of the triplet states of the photosensitizers will also affect phototransformation rates. Like PGL, transformations of 2,3-DMP and 2,3,5-TMP were accelerated by the presence of pterin, indicating that these phenols were also transformed via photosensitized pathways in seawater. However, PGL, which has the lowest pK_a of the three phenols, had faster transformation rates under identical irradiation, indicating the importance of ambient pH and degree of dissociation to phenoxides in phenol transformations in seawater (Lin and Carlson, 1991). These relative reactivity differences were observed in natural SFC samples and in pterin-amended samples and were consistent with pK_a-dependent reactivities of these and other phenols observed during natural DOM-sensitized transformations in freshwater (Faust and Hoigne, 1987) and seawater (Lin and Carlson, 1991). These similar reactivities in natural samples and in samples supplemented with photosensitizers (e.g. pterin) suggest similar transformation mechanisms in each case.

In seawater without additions of pterin, natural chromophoric compounds acted as photosensitizers. The fact that phenol transformations rates in SFC samples were always greater than in SBW samples even though light conditions were identical indicates enhanced photosensitizing capability due to the DOM and photosensitizer enrichments in the SFC samples. Terrestrial humic substances have often been identified as effective photosensitizers in freshwater and seawater solutions (Zika, 1977; Cooper, et al, 1989), but marine humic-type substances are not a large fraction of marine DOM and may differ significantly from terrestrial humic substances (Harvey et al., 1983). Most organic compounds in natural waters at ambient pH are transparent to wavelengths greater than 300 nm, whereas pterin has an absorption maxima around 350 nm. The triplet excited state of pterin also has an energy level of 55 Kcal / mol (Chahidi et al., 1981), greater than the 1^O_2 formation threshold (22.5 Kcal / mol, Arnold et al., 1968). Therefore, molecules similar to the pteridines,
evolved from biological sources with similar fluorescence properties and similar nitrogen-containing heterocyclic structures or at least with similar absorption properties and triplet state energies, are likely to be the dominant natural photosensitizers inducing $^{1}\text{O}_2$ production in seawater (Landymore and Antia, 1978; Chahidi et al., 1981, Momzikoff et al., 1983b).

Fluorescent compounds such as pterin and their derivatives have been identified as components of marine DOM at low concentrations (Dunlap and Susic, 1985; Mopper and Zika, 1987), and have been found to decompose in seawater exposed to sunlight (Dunlap and Susic, 1986; Mopper and Zika, 1987). Such decompositions indicate photoreactivity which may include the production of $^{1}\text{O}_2$ and induction of phenol transformations. Because slicked surface microlayers contain an abundance of microorganisms (e.g. Carlson et al., 1988; Cullen et al., 1989), some of which may release these fluorescent compounds as normal metabolites (Gail and Momzikoff, 1975; Baker et al., 1981) or due to stress imposed by the microlayer environment, and an abundance of other hydrophobic materials, slicks may be accumulation zones for photosensitizers. However, no accumulation of pteridine-like fluorescent compounds in surface microlayers has yet been reported, so it is difficult to quantify or evaluate their importance as photosensitizers in sunlit surface seawater and surface microlayers. The strong correlations between ultraviolet absorbance enrichments (indicative of DOM) and chlorophyll a fluorescence enrichments observed in surface slicks (Carlson et al., 1988, Cullen et al. 1989) may suggest the presence of photoreactive fluorescent heterocyclic compounds if the latter are associated with or derived from chlorophyll-containing organisms. Transformation rates of PGL in slick samples have been shown to increase with the degree of UV absorbance enrichment (Lin and Carlson, 1991), again suggesting accumulation of natural photosensitizers in surface slicks.

3.5.2. Phototranformation Mechanisms

As mentioned above, the evidence for photosensitization (reduction of phototransformations when oxygen was removed) and the known presence of abundant oxygen in surface seawater indicates that phenol transformations involved $^{1}\text{O}_2$. The existence of $^{1}\text{O}_2$ in freshwater and seawater has been demonstrated by use of several quenching techniques (Zepp et al., 1977; Momzikoff et al., 1983b). Of the commonly-used quenchers, DABCO has been reported as especially effective at
deactivating chemical, thermal, or photochemical $^{1}\text{O}_2$ in aqueous solutions (Quannes and Wilson, 1968; Zepp et al., 1977). In our work, the addition of DABCO decreased phenol phototransformation, indicating the involvement of photo-produced $^{1}\text{O}_2$ in seawater phototransformations. We assume that DABCO significantly reduced steady state $[^{1}\text{O}_2]$ concentration in our samples, thereby reducing the experimental transformation rate constants ($k_{\text{exp}}$'s) for the three phenol tracers so that no transformations of 2,3-DMP and 2,3,5-TMP occurred while only slight transformations were observed for PGL (16% of total $k_{\text{exp}}$ for PGL). Concentrations of DABCO greater than 1.0 mM did not further reduce transformation of PGL, indicating that 1.0 mM DABCO was sufficient to deactivate all photo-produced $^{1}\text{O}_2$ in the irradiated solutions and to reduce $[^{1}\text{O}_2]_{ss}$ to an insignificant level. The slight transformation of PGL in the presence of high DABCO concentrations may indicate other minor phototransformation pathways. Direct photolysis is possible but unlikely because of the transparency of the phenols to sunlight. Direct reaction between the phenols and natural photosensitizer triplets might have occurred before the triplets underwent electron transfers (Type 1 processes) (Foote, 1979). Rate constants for PGL transformation by direct interaction with photosensitizer triplets ($k^3_{ps}$) estimated from PGL kinetics in SFC sample in the presence of 1 mM DABCO would be about 0.0118 min$^{-1}$, only about 16% of total $k_{\text{exp}}$ in an unquenched SFC sample. Neither of the alkylphenols showed any evidence of reaction mechanisms not quenched by addition of DABCO. In addition to quenching $^{1}\text{O}_2$ generated from natural photosensitizer triplets in natural SFC samples, addition of DABCO also quenched the $^{1}\text{O}_2$ presumed to be generated from pterin triplets when pterin was added to samples, confirmation that 1.0 mM DABCO was sufficient to quench excess $^{1}\text{O}_2$ generated by triplet states of fluorescent compounds such as pterin even at concentrations of 2.5 $\mu$g /l. The similar effect of DABCO in natural and pterin-amended samples again suggests photosensitized transformations of phenols via $^{1}\text{O}_2$ mechanisms. If physical quenchers like DABCO or other amines exist at significant concentrations in seawater, photochemical reactivity in a given volume will depend on the balance between number and efficiency of photosensitizers and the number and effectiveness of quenchers.

Because most ground state molecular structures are singlet configuration, $^{1}\text{O}_2$ is more reactive than oxygen in its ground state ($^{3}\text{O}_2$) in inducing oxidations in aqueous solutions. However, high reaction selectivity of $^{1}\text{O}_2$ means that only a few groups of electron-rich compounds will react with $^{1}\text{O}_2$. Depending on substituent groups,
phenolic compounds with electron-rich molecular structures of conjugated bonds are capable of reacting with $^{1}\text{O}_2$ via phenoxy radical formation or via 1,4-cycloaddition to form hydroperoxides (Saito and Matsuura, 1979). For example, reaction of TMP with $^{1}\text{O}_2$ has shown to occur via formation of phenoxy radicals (Thomas and Foote, 1978). These unstable intermediates, like other free radicals, may undergo further coupling reactions to form more complex products. Other biochemical compounds such as phenolic amino acids and conjugated unsaturated fatty acids are believed to undergo photocondensation reactions induced by $^{1}\text{O}_2$ in surface films on seawater, giving rise to condensates with some characteristics of humic acids (Harvey et al., 1983; Momzikoff et al., 1983a). Also, UV irradiation of algal phloroglucinol polymers in seawater resulted in products with characteristics of further polymerization (Zika, 1977). These results may suggest the transformation products of phenolic compounds in surface seawater.

Besides $^{1}\text{O}_2$, organic peroxy radicals (ROO·) are also potentially-important photo-produced transients due to their high steady-state concentrations (Mill et al., 1980), and they have been proposed to be involved in photo-oxidation of several alkylphenols in freshwater (Faust and Hoigne, 1987). Attention has recently been focussed on organic peroxy radicals in seawater (Blough, 1988; Zafiriou et al., 1990) and their existence in seawater has been verified (Kieber and Blough, 1990). It has been reported that nitroxides are able to trap carbon-centered radicals (R·) in determination of biochemical pathways involving organic radicals (Nigam et al., 1976; Beckwith et al., 1988). However, addition of a nitroxide (3-AMP) to our samples did not inhibit the transformation of PGL in either oxygen-saturated or reduced oxygen conditions. The nitroxide is thought to react rapidly with R· before the radicals undergo further reactions with dissolved oxygen to form ROO·, the potential transient for reaction with phenols in seawater (Kieber and Blough, 1990). However, the reduction of ROO· (the presumed result of trapping R· with 3-AMP) increased phototransformation rates of PGL, with higher 3-AMP concentrations causing higher transformation rates. Although we are not aware of mechanisms by which 3-AMP might enhance phenol phototransformations, our results do indicate that ROO· were probably not involved in the transformation of phenols in seawater under sunlight.

Because our data provided direct and indirect evidence for $^{1}\text{O}_2$ involvement in the photosensitized transformations of phenols in seawater, we conclude that sunlight-
generated \(^1\text{O}_2\) reacts directly with phenolic compounds (and perhaps with other electron-rich organic compounds) in surface microlayers and in sunlit surface seawater. The half-lives of PGL in SFC samples calculated from the overall rates of these transformations, assuming 1.0 \(\mu\)M concentrations and mid-day sunlight, were less than 2 hours, exactly as observed by Lin and Carlson (1991). The rate of reaction between the phenols and \(^1\text{O}_2\) can also be estimated, assuming steady-state values of \(^1\text{O}_2 = 2 \times 10^{-14}\) M. We determined these second-order rate constants to be 8.0, 3.5, and 0.9 \(*\) \(\times 10^7\) for reactions between PGL, 2,3,5-TMP and 2,3-DMP, respectively, and \(^1\text{O}_2\). The steady-state value of \(^1\text{O}_2\) was given by Haag and Hoigne (1986) for surface coastal seawater under midday sunlight (1000 W m\(^{-2}\)). We used the maximum of their suggested range of values because of the presumed presence of abundant photosensitizers in surface microlayers and because of high irradiation levels at the immediate surface. Actual values for \(^1\text{O}_2\) in an intense slick on a bright day might be higher yet. Our estimated \(k_r\)'s for all three compounds are somewhat larger than \(k_r\) values for phenol and cresol reaction with \(^1\text{O}_2\) in freshwater estimated by Scully and Hoigne (1987). These difference between our tracers (PGL, 2,3-DMP, and 2,3,5-TMP) and phenol or cresol are consistent with slower transformation rates of phenol and cresol in freshwater and seawater (Faust and Hoigne, 1987; Lin and Carlson, 1991). Thus degradation rates of any of these phenols in slicks at the ocean surface will be determined by concentrations at or supply of the phenols to the surface and steady-state concentrations of \(^1\text{O}_2\), which in turn are a function of light and photosensitization. It is clear that some or all of these factors are maximal in surface slicks.

3.6. Summary

Our results indicate that absorption of sunlight by compounds such as pterin in seawater can lead to rapid photosensitized transformations of phenolic compounds, probably via energy transfer processes from photo-excited triplet states of the photosensitizers. Because oxygen is the predominant acceptor of triplet state energy in oxygenated waters and because transformations of tracer phenols were reduced when oxygen was reduced or when \(^1\text{O}_2\) quenchers were present, regardless of photosensitizer concentrations, we conclude that the major reactive transient acting on phenols or compounds of similar chemistry is \(^1\text{O}_2\). Rates of reaction between the tracer phenols and \(^1\text{O}_2\) in seawater were consistent with previous estimates in freshwater. Faster transformations of tracer phenols in SFC samples than in SBW
samples at the same light intensities suggests that photosensitizers are more abundant in those samples. Other photo-produced transients such as ROO· seemed not to affect tracer phenol transformations in SFC samples, although minor direct reactions between photosensitizer triplets and phenol may have occurred.

ACKNOWLEDGEMENTS

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4. CONCLUSIONS

The goals of this thesis have been threefold: understanding sunlight-induced transformation kinetics of phenolic compounds in surface seawater, determining mechanisms of transformations of phenolic compounds in surface seawater, and estimating surface microlayer photoreactivity of photoreactive compounds such as phenolic compounds under surface sunlight.

The information obtained, or reinforced, concerning characteristics of transformation kinetics and mechanisms of phenolic compounds in surface seawaters can be summarized as follows:

(1) Photochemical reactivities (in term of transformation rates of the phenols) of surface microlayers, especially collected from surface slicks, were always higher than subsurface bulkwaters under surface sunlight intensities.

(2) Transformations in the absence of light were very slow in seawater in comparison with samples irradiated with sunlight under the same experimental conditions. Transformations were also very slow in pure distilled water in comparison with seawater under the same light conditions.

(3) Sunlight-induced transformations of phenols were rapid photochemical processes, with half-lives for the phenols under mid-day surface sunlight of hours in surface microlayers samples or in subsurface bulkwater samples.

(4) Phenol transformations were DOM-dependent, and surface microlayer rates relative to subsurface rates were correlated with ultraviolet (280 nm) enrichment of surface slicks.

(5) Phenol transformations were accelerated by addition of pterin as photosensitizer, increasing directly with amounts of pterin added.

(6) Phenol transformations were inhibited by removing dissolved oxygen. The addition of pterin did not enhance transformation rates in oxygen-free samples.

(7) Phenol transformations were significantly inhibited by addition of \(^{1}\text{O}_2\) quenchers, NaN\(_3\) and DABCO, although slight transformation of PGL still occurred even at high concentrations of DABCO.

From these results, conclusions can be drawn to describe the sunlight-induced transformations of phenolic compounds in surface seawater. In general, sunlight-transparent phenolic compounds are not directly sensitive to natural surface sunlight. Instead, a fraction of DOM chromophoric components appear to absorb sunlight and
transfer energy from photo-excited triplets to dissolved oxygen molecules to form $^{1}\text{O}_2$. Subsequent transformations of phenolic compounds under surface sunlight are actually photosensitized processes with chromophoric components acting as natural photosensitizers. At low or zero concentrations of natural photosensitizers, photosensitized transformations were extremely slow. Pterin was able to sensitize phenol transformations, indicating that pterin and similar molecules in surface seawaters may be effective natural photosensitizers and may be involved in transformations of phenolic compounds. In surface seawater, especially in organic-rich surface microlayers, high steady-state concentrations of $^{1}\text{O}_2$ can be expected. Due to its high selective reactivity toward phenols, $^{1}\text{O}_2$ may react directly with the phenols, leading to photo-oxidation mechanisms for phenols in seawater. Other reactive photo-produced transients may also induce transformations of phenols. However, the results of this work indicate that reactions of phenolic compounds with $^{1}\text{O}_2$ overwhelm other reactions between reactive transients and phenols in sunlit surface seawater. Thus, even relatively abundant transients such as organic peroxy radicals (ROO') seem less important in cases where phenolic compounds are photochemically altered. In sum, as surface microlayer components, phenolic compounds can be involved in rapid photochemical transformation processes and removed from surface microlayers at a high rate, although they are not directly sensitive to sunlight.

Reactions between $^{1}\text{O}_2$ and the phenols were rapid processes, as reflected in measured pseudo-first-order rate constants in both surface slick samples and subsurface bulkwater samples. The estimated half-lives of phenols in surface seawater were on the order of hours, suggesting short residence times for phenolic compounds in surface seawater. Enhanced surface microlayer photochemical reactivity toward the phenols was attributed to enrichments of dissolved organic materials whose chromophoric components absorbed sunlight to produce high concentrations of $^{1}\text{O}_2$. These high concentrations of $^{1}\text{O}_2$ in surface microlayer samples resulted in rapid transformation rates of phenols relative to subsurface bulkwater samples. In addition to the steady-state concentrations of $^{1}\text{O}_2$, structures of the phenolic compounds affected transformation rates. It appeared that phenoxide formation at seawater pH was a determining factor for reaction rates. For three tracer phenols the reaction order was PGL > 2,3,5-TMP > 2,3-DMP. Phenols with lower pK_a such as PGL usually have highest reactivity toward $^{1}\text{O}_2$ in seawater. On the basis of pseudo-first-order rate constants in surface slick samples, second-order
rate constants with respect to the phenols and $^1O_2$ were estimated by assuming a steady-state concentration of $^1O_2$ ($2 \times 10^{-14}$ M) in surface microlayers. However, there were obvious variations of measured pseudo-first-order rate constants of PGL in slick samples collected from different locations or on different days. Thus the estimated rate constants for phenolic compounds and $^1O_2$ could have a determination error of the same range as variation of pseudo first-order rate constants.

4.1 Application to Oceanic Conditions

A review resulting from the 1987 CHEMRAWN Workshop (Waite et al., 1988) provides clear up-to-date evidence of the importance of photochemical processes in the upper ocean. Many efforts have been concentrated on detecting low molecular weight products such as gases or aldehydes in bulk water, while the overall DOM degradation rates and any residual organic materials from such photochemical processes remain largely unknown. The air-sea interface accumulates dissolved organic materials from the ocean and other potentially-reactive components from the atmosphere so that its chemical composition is considerably different from bulk waters (Williams et al., 1986). It is also exposed to the full solar spectrum of light arriving at the surface. For these reasons, marine surface microlayers should be among the most photochemically-active regions of the ocean. Surface microlayer photochemistry will be underestimated by simply extrapolating near-surface transformation rates to surface sunlight intensities. The kinetic data for phenolic transformations in this work are the first to be measured directly in surface microlayer samples, and indicate that rapid photochemical processes are taking place in surface microlayers probably because photo-produced transients are highly concentrated or rapidly supplied. These measurements of sunlight-induced transformation rates can be applied to estimate residence times of phenolic compounds in oceanic conditions. By comparing reactivities with these phenols, residence times of other components of surface microlayers can be also predicted. This information may be useful in establishing models to predict fates of DOM and distribution of photoproducts in the marine environment.

As mentioned, $^1O_2$ may react directly with phenols to induce photochemical changes. Other biochemical compounds such as amino acids, proteins or nucleic acids may also be attacked by $^1O_2$ in the marine environment, resulting in negative impacts on biological activities and the marine ecosystems varying from death (for
microbes and small organisms) to reduced growth or photosynthesis rates (in plants) to serious diseases (in large animals) (Dahl, 1989). The mechanisms by which tracer phenols react with $^1$O$_2$ indicate that natural phenolic compounds may serve as molecular probes to detect generation and steady-state concentrations of $^1$O$_2$ in the marine environment. Such probes may be important if blue shifts of the solar spectrum lead to increases in steady-state concentrations of $^1$O$_2$ and to increased phototoxicities of the marine environment.

4.2 SUGGESTIONS FOR FUTURE WORK

In fact, there are still problems involved in estimating large scale residence times of phenolic compounds in oceanic conditions because: (1) the sources and supply rates of natural phenols in the upper ocean are unknown; (2) the absorption characteristics of natural photosensitizers and their quantum yields for $^1$O$_2$ throughout sunlight spectrum are unknown; (3) the physical characteristics of seawater exchange between surface microlayer and subsurface bulkwaters are unknown. In addition, detection of the specific products of phenol photochemical transformations is necessary and important though extremely difficult to do. Much work will be required to identify or quantify unknown products, processes or rates. It is clear from this work that surface microlayers, especially slicked surface microlayers, are an excellent region in which to conduct such work.


