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The role of carbonate radical in limiting the persistence of sulfur-containing chemicals in sunlit natural waters

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Abstract

Carbonate radical ($\cdot CO_3^-$) is a selective oxidant that may be important in limiting the persistence of a number of sulfur-containing compounds in sunlit natural waters. Thioanisole, dibenzothiophene (DBT), and fenthion were selected to investigate the degradation pathway initiated by $\cdot CO_3^-$; electron-rich sulfur compounds are particularly reactive towards the $\cdot CO_3^-$. Using HPLC, GC, GC–MS and LC–MS for structural confirmation, the major photodegradation products of thioanisole and DBT were the corresponding sulfoxides. The sulfoxide products were further oxidized through reaction with $\cdot CO_3^-$ to the corresponding sulfone derivatives. Fenthion showed a similar pathway with appearance of fenthion sulfoxide as the major product. The proposed mechanism involves abstraction of an electron on sulfur to form a radical cation, which is then oxidized by dissolved oxygen. Each of the sulfur probes were further investigated in a sunlight simulator under varying matrix conditions. The highest rate constants occurred in the $\cdot CO_3^-$ matrix, and the lowest occurred in a matrix of dissolved organic carbon (DOC) and bicarbonate. In synthetic and natural field water, thioanisole photodegraded faster than under direct photolysis, with half-lives of 75.1 and 85.8 min, respectively. Fenthion photodegraded more rapidly than thioanisole. DBT photodegraded rapidly in a $\cdot CO_3^-$ matrix with a half-life of 24.8 min, while the half-life of direct photolysis was 350 min. Photodegradation products of each compound were also investigated. Ultimately, $\cdot CO_3^-$ was found to contribute toward the photodegradation of sulfur-containing compounds in natural waters.

Keywords: Photolysis; Thioanisole; Fenthion; Dibenzothiophene

1. Introduction

The persistence of chemical pollutants in natural waters is determined by the ability of such waters to cleanse themselves of xenobiotics. Sunlight-induced direct and indirect photoreactions provide an important sink for chemical pollutants in such environments; direct photolysis contributes only partially to these sunlight-induced reactions. The rate constants for direct photolysis in sunlight of a specific chemical require information regarding the absorption spectrum of the chemical, the quantum yield of the process (ϕ, the efficiency), and the light intensity as a function of wavelength, latitude, season, and time of day (Zepp and Cline, 1977). Indirect photolysis involving photochemically produced reactive chemical transients is also an important fate for these pollutants (Zepp, 1991). Such transients include alkylperoxy, hydroxyl, and carbonate radicals ($\cdot CO_3^-$), singlet oxygen, aqueous electrons, and triplet states. The nature and steady-state concentration of these transients strongly depend upon the composition of the water, particularly on the concentrations of dissolved organic matter, nitrate, nitrite, and trace metals. The rate of indirect photolysis can be predicted from the second-order

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rate constant for its reaction with the transient and the steady-state concentration of the transient (Zepp, 1991).

$\cdot CO_3^-$ is a sunlight-generated secondary radical produced from the reaction of hydroxyl radical $\cdot(OH)$ with either carbonate or bicarbonate ions. In sunlit natural waters, the $\cdot OH$ is formed primarily through the photolysis of nitrate (Hagg and Hoigné, 1985; Zepp et al., 1987); hydroxyl can also be formed through the photolysis of H_2O_2 (Larson and Zepp, 1988), nitrite (Zafiriou, 1974), and dissolved organic carbon (DOC) (Mill et al., 1980) although these are generally considered minor pathways. $\cdot CO_3^-$ is a more selective oxidant than $\cdot OH$ which leads to relatively higher steady-state concentrations (Zepp, 1991); the concentration of $\cdot CO_3^-$ will be a function of hydroxyl production rates, and the relative proportion of scavenging by DOC or carbonate/bicarbonate.

Larson and Zepp (1988) investigated the reaction pathway of $\cdot CO_3^-$ with a number of aromatic amine compounds and concluded that, particularly for electron-rich systems, $\cdot CO_3^-$ reacts rapidly by electron transfer. The second-order rate constant of $\cdot CO_3^-$ was high for indole and its derivatives such as tryptophan ($k > 10^8$ M^{-1} s^{-1}) (Chen and Hoffman, 1974). As a selective oxidant, $\cdot CO_3^-$ may play an important role in oxidizing sulfur-containing compounds with a rate constant at 10^6 to 10^7 M^{-1} s^{-1} (Chen and Hoffman, 1973), thus contributing to their transformation. Ultimately, $\cdot CO_3^-$ may also affect the cycling of naturally occurring sulfur compounds in aqueous systems. Therefore, it is important both to measure the reactivity and to understand the pathways of a $\cdot CO_3^-$ reaction with sulfur-containing compounds.

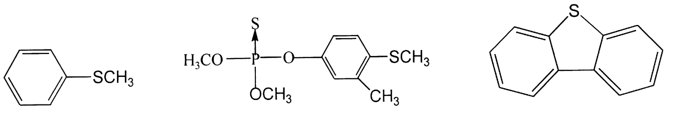
The compounds selected for this investigation were thioanisole, fenthion, and dibenzothiophene (DBT) (Fig. 1). Thioanisole was selected to identify the reaction pathways of $\cdot CO_3^-$ towards an aromatic sulfur compound with structural similarities to an organophosphorous insecticide, fenthion (Cabras et al., 1991). Once used extensively as an effective insecticide, fenthion was classified by the US EPA as a restricted use pesticide (RUP) on the basis of its toxicity (Kamrin, 1997). Five metabolites of fenthion have been isolated in animals and plants (Cabras et al., 1993). The fenthion sulfoxide and fenthion sulfone were observed as fenthion photolysis products on fruit surfaces (Minelli et al., 1996). Degradation kinetics of fenthion in different waters under various environmental conditions have previously been investigated (Lartigues and Garrigues, 1995). Fenthion degraded much faster under sunlight conditions than in the dark, with the following half-lives at 22°C: 42 d in darkness and 2 d under sunlight for river water at pH 7.3; 26 d in darkness and 5 d under sunlight for sea water at pH 8.1. In estuarine waters, the half-lives of fenthion and its major transformation product, fenthion sulfoxide were reported to be 4.6 and 6.9 d, respectively (Lacorte et al., 1995). DBT is found in fossil fuels, the fuel value of which is partly lowered due to the high organic sulfur content which, upon combustion, can release sulfur dioxide into the atmosphere, causing acid rain. A desulfurization process for DBT through a combination of photochemical reaction and liquid–liquid extraction has been investigated (Hirai et al., 1997). During the desulfurization of DBT by *Rhodococcus* sp. strain IGTS8, the formation of key metabolites, including dibenz[c,e][1,2] oxathiin 6-oxide (sultine) and dibenz[c,e][1,2] oxathiin 6,6-dioxide (sultone) were investigated through extensive GC/FTIR/MS analysis (Olson et al., 1993). The metabolites from the biodesulfurization of DBT in bitumen were also reported by using SPME/GC–MS (Macpherson et al., 1998).

Our hypothesis was that $\cdot CO_3^-$ would contribute to the natural cleansing of these model pollutants from sunlit natural waters. Our objectives were to identify the major photodegradation products of these selected aromatic sulfur-containing compounds and measure their reactivities under varying natural and synthetic field water (SFW) conditions to reveal the relative importance of $\cdot CO_3^-$ to limiting their persistence.

2. Materials and methods

2.1. Chemicals

Thioanisole, methyl phenyl sulfoxide, DBT and dibenzothiophene sulfone were obtained from Aldrich (Oakville, ON), as well as sodium nitrate, sodium carbonate and sodium bicarbonate. Fenthion was obtained from Chem Service (West Chester, PA). The intermediate photodegradation products such as fenthion sulfone were synthesized from slightly modified published methods (Cabras et al., 1991). An aqueous 0.15 M solution of $KMnO_4$ was added to a solution of fenthion in



Thioanisole **Fenthion** **Dibenzothiophene**

Fig. 1. Chemical structures of selected compounds.

acetic acid. The reaction mixture was then agitated for 12 h, diluted with water and extracted with chloroform. Using silica gel column chromatography with 60% ethyl acetate and 40% hexane as the mix solvent, the crude fenthion sulfone residue was purified to yield a white crystalline solid; methyl phenyl sulfone was synthesized through similar procedures. Fenthion sulfoxide and DBT-sulfoxide were synthesized, respectively, from fenthion and DBT in methanol by reaction with equimolar H_2O_2/SeO_2. The reaction mixture was cleaned up using silica gel column chromatography. DOC was obtained by photobleaching Aldrich humic acid in direct sunlight for 2 weeks. The mixture was diluted with HPLC grade water to a final concentration of 50 mg carbon/l as determined by a DOC analyzer (OI Corporation Model 1010 TOC analyzer); final absorbance of the solutions was 0.43 in a 1 cm path length at 370 nm. The stock solution was kept in the refrigerator with no headspace in the container.

2.2. Photolysis

Irradiation of the sample solutions in quartz test tubes was carried out in a sunlight simulator (Atlas Suntest CPS). $\cdot CO_3^-$ was generated from the photolysis of 0.1 M Na_2CO_3 and 3 mM H_2O_2 (Larson and Zepp, 1988) in order to determine reaction pathways. SFWs with varying concentrations of nitrate, DOC, and bicarbonate were then run at fixed positions in the photoreactor (Table 1); the sunlight simulator was set at a maximum irradiance level of 765 W/m^2. Dark controls were run excluding light, while direct photolysis was run in distilled/deionized HPLC grade water; all experiments were run in duplicate.

2.3. Field water analysis

A Lake Huron water sample served as our reference field water. DOC was determined as previously described while nitrate and bicarbonate ions were analyzed via ion-exchange chromatography with a Perkin-Elmer series 200 IC pump and an Alltech 550 conductivity detector, equipped with an ERIS 1000 HP Autosuppressor. The column was an IonPac AS 14 4 mm and IonPac AG 14 4 mm (Dionex). The gradient was initiated and held for 6 min at 4% 50 mM borate and 96% deionized water followed by a linear increase to 30:70 (borate:deionized water) over 18 min; the instrument was allowed to re-equilibrate for 5 min at initial conditions.

2.4. Analysis

Photodegradation products were extracted (~50 ml) and concentrated by solid-phase extraction (500 mg C18 SPE, Supelco), and spike recovery of each analyte was above 80%. The concentrated samples were then analyzed through reverse phase HPLC (Waters 600S) with a 996 PDA detector (C18 column; 250 mm X ID 4.6 mm) and GC using a Perkin-Elmer Autosystem XL GC with an FPD detector analysis. The GC column was equipped with Supelco MDN-5 column (0.25 mm × 30 m; 0.25 μm film thickness) (split ratio: 5:1) and injector temperature of 250°C; initial temperature was 50°C for 1 min, followed by a 10°C/min ramp to 200°C, with a final 1 min at 200°C. Hydrogen was used as carrier gas with a flow rate of 5 ml/min. The flow rates of air and hydrogen were 90 and 75 ml/min, respectively. Structural confirmation was obtained by GC–MS (TurboMass) or LC–MS (PE Sciex API 3) in comparison with authentic standards. Kinetic analysis of each probe during photolysis was obtained through direct injection onto the HPLC-PDA under isocratic conditions with acetonitrile–water (varying ratios) at a flow rate of 1.0 ml/min; all injections were conducted in triplicate.

3. Results and discussions

3.1. Reaction pathways

Fenthion and thioanisole both react rapidly with $\cdot CO_3^-$ with a second-order rate constant of 2.0×10^7 and 2.3×10^7 M^{-1} s^{-1}, respectively, which we previously measured using a new competition kinetic system (Huang and Mabury, 2000). Methyl phenyl sulfoxide was

Table 1
Synthetic field waters and photolysis solutions

Matrix	pH	Components
DI water	6.50	Pure DI water
High $\cdot CO_3^-$	11.05	0.04 M Na_2CO_3 + 1.5 mM H_2O_2
Biocarbonate radical	8.30	500 ppm HCO_3^- + 50 ppm NO_3^-
Synthetic field water	8.30	5 mg/l DOC + 500 ppm HCO_3^- + 50 ppm NO_3^-
DOC/bicarbonate	8.28	5 mg/l DOC + 500 ppm HCO_3^-
DOC/nitrate	6.75	5 mg/l DOC + 50 ppm NO_3^-
Filtered Lake Huron water	8.10	2.6mg/l DOC + 105 ppm HCO_3^- + 6.2 ppm NO_3^-
Dark control matrix	8.30	500 ppm HCO_3^- + 50 ppm NO_3^-

identified by reverse-phase HPLC-PDA as the major product after the irradiation of thioanisole with $\cdot CO_3^-$ (Fig. 2); the UV spectrum and retention time of the unknown peak matched those for an authentic standard of methyl phenyl sulfoxide. The reacted sample was extracted and concentrated through C-18 solid phase extraction (SPE) cartridge and was subsequently run on a GC-FPD detector to show clearly the presence of the sulfoxide product; final structural confirmation was provided by GC–MS with *m*/*z* 140 (M^+, 100), 125 (95), 97 (40) and 77 (53). Methyl phenyl sulfoxide was run under the same conditions and yielded slow conversion to the sulfone (Fig. 2), which was confirmed by HPLC-PDA, GC–FPD and GC–MS. Direct injection of thioanisole photolysate into an LC–MS (negative ion mode) tentatively identified benzenesulfonic acid as a minor product. A molecular ion peak at *m*/*z* 157 and fragment at *m*/*z* 79.6 of SO_3^- were observed, which were the same as observed for a standard injection.

Fenthion irradiated with $\cdot CO_3^-$ for 15 min resulted in many observed peaks in the HPLC chromatogram. Fenthion sulfoxide was the major product, which was similar to previous reports of photolysis in environmental matrices (Cabras et al., 1991; Lacorte et al., 1995). Further reaction with $\cdot CO_3^-$ yielded fenthion sulfone; the presence of both compounds was confirmed using UV and GC–MS spectra. Elucidation of the reaction pathways of fenthion with $\cdot CO_3^-$ were complicated, due to the likely hydrolysis of the photo-oxidized products. In a previous work we showed each of the metabolites of fenthion to hydrolytically degrade faster than the parent compound (Huang and Mabury, 1999).

Similarly, DBT irradiated with $\cdot CO_3^-$ for 15 min yielded DBT-sulfoxide, identified through HPLC-PDA

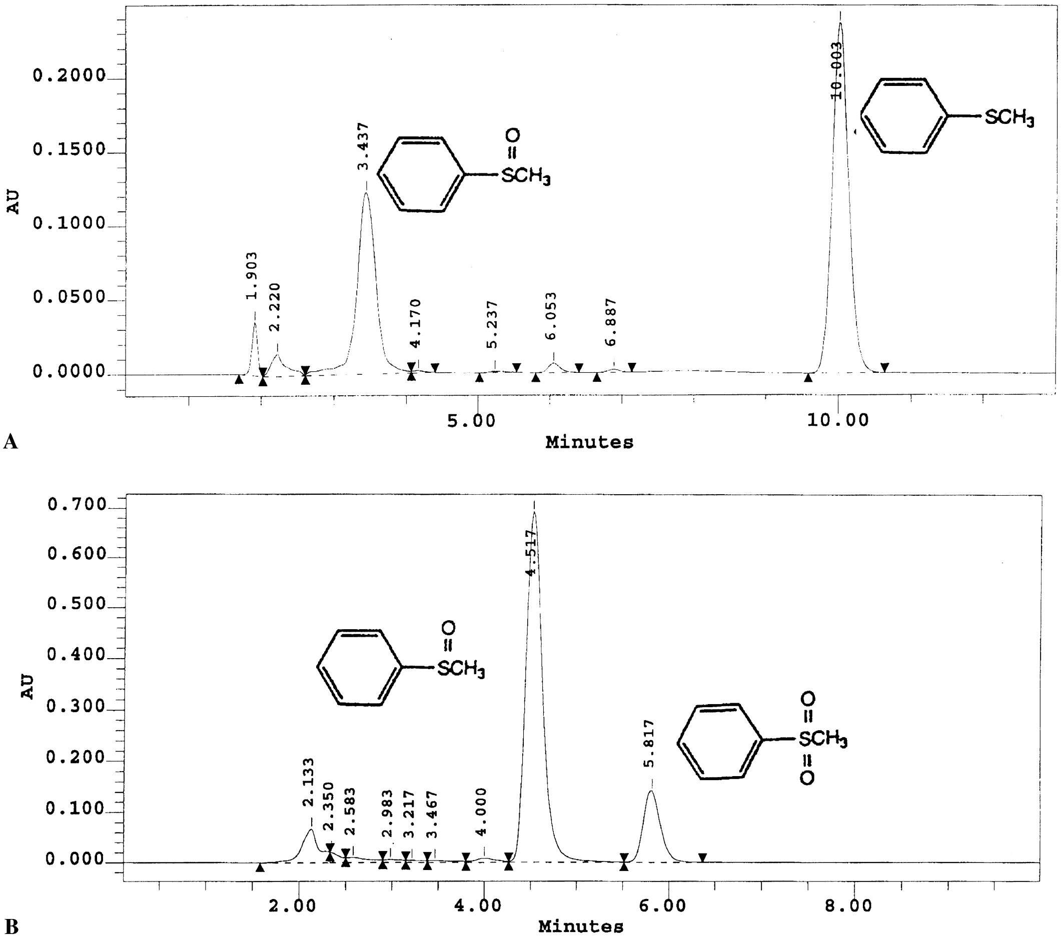


Fig. 2. Thioanisole photoreaction with $\cdot CO_3^-$ for 1 h; the sample was concentrated through SPE and separated by HPLC (60% acetonitrile and 40% water as mobile phase; flow rate = 1.0 ml/min) (A). Methyl phenyl sulfoxide photoreaction with $\cdot CO_3^-$ for 1.2 h; the sample was concentrated through SPE and separated through HPLC (40% acetonitrile and 60% water as mobile phase; flow rate = 1.0 ml/min) (B).

and structurally confirmed through GC–MS, as the major product; DBT-sulfone was confirmed as the product of $\cdot CO_3^-$ reaction with DBT-sulfoxide. Similar metabolites were also reported in the biodesulfurization of DBT in bitumen (Macpherson et al., 1998). All primary reaction pathways of the selected compounds with the $\cdot CO_3^-$ are shown in Fig. 3.

3.2. Reaction mechanism

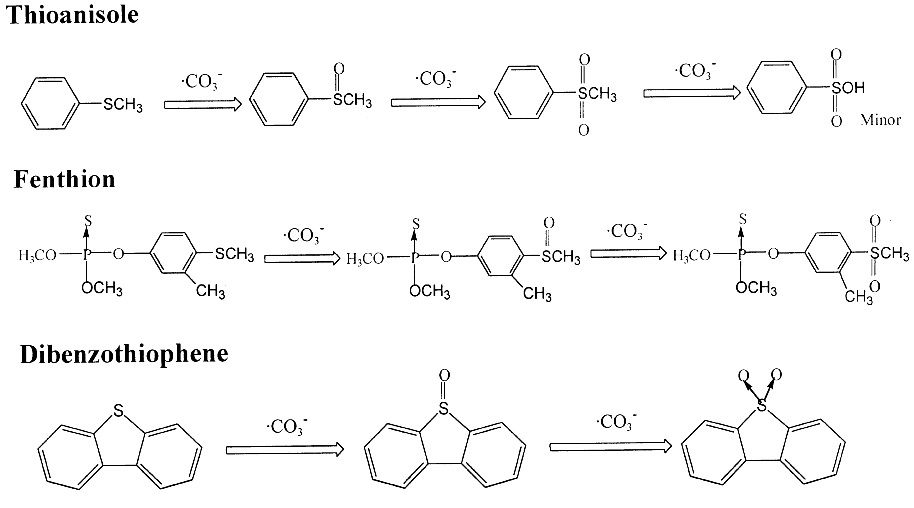
The most reactive site of the selected aromatic compounds when reacting with $\cdot CO_3^-$ occurred at the sulfur atom. The primary reaction pathway of the compounds selected indicated primary conversion to the corresponding sulfoxide followed by slow production of the sulfone. A study of aquatic photodegradation of albendazole under sunlight showed similar metabolites of albendazole sulfoxide and sulfone (Weerasinghe et al., 1992). Draper and Crosby (1984) investigated solar photo-oxidation of sulfur-containing pesticides in dilute hydrogen peroxide. Electron transfer reactions were proposed to initiate sulfur oxidation observed in the thiocarbamates molinate and thiobencarb with sulfoxide formation resulting from radical coupling of dissolved oxygen in water. This mechanism may partially explain results in this investigation with $\cdot CO_3^-$ as the initiator of the electron transfer that ultimately yields the corresponding sulfoxide and sulfone. Under direct photolysis conditions in DI water, relatively small amounts of sulfoxide and sulfone were produced, which presumably occurred through a similar mechanism.

Under high $\cdot CO_3^-$ conditions, sulfoxide formation could also proceed through O^- transfer from a second $\cdot CO_3^-$. Initial electron transfer from the sulfur atom to $\cdot CO_3^-$, as described above, occurs to form the cation radical. The second step involves O^- transfer from a second $\cdot CO_3^-$ to the sulfur cation radical. It was shown that $\cdot CO_3^-$ could react with other radicals via the transfer of an O^- ion, and O^- transfer to molecules with closed electron shells has not previously been observed (Lilie et al., 1978). The reaction of $\cdot CO_3^-$ probably occurred through both mechanisms. However, under realistic natural water conditions, the steady-state concentration of $\cdot CO_3^-$ would be too low for O^- transfer to be significant in comparison to dissolved oxygen.

3.3. Persistence in different matrices

During a cloudless summer noon hour, surface waters receive approximately 1 kW/m^2 of sunlight. The photoreactor simulated sunlight wavelengths with a fixed irradiance level at 765 W/m^2. A suite of SFWs (Table 1) was used to delineate more clearly the putative role of $\cdot CO_3^-$ contributing to the natural cleansing of sulfur-containing chemical pollutants in field waters. The amount of DOC was about 5 mg/ml, which is a reasonable range for most field waters. DOC can not only contribute to the production of transients in natural waters including ·OH, but can also scavenge the ·OH with a second-order rate constant of 2.5×10^4 (l/mg DOCs) (Larson and Zepp, 1988). The rate constants and half-lives of selected compounds in different matrices are shown in Table 2; the rate constants for duplicate runs had relative errors less than 5%.

The pseudo-first-order photoreaction of thioanisole in the different waters is shown in Fig. 4. In the dark control solution at pH 11.0, there was no apparent change of concentration over the time of the experiment. In contrast with direct photolysis in DI water, the most rapid photoreaction occurred in the matrix with a


Thioanisole

Fenthion

Dibenzothiophene

Fig. 3. Primary reaction pathways towards $\cdot CO_3^-$.

Table 2
Photoreaction rate constants and half-lives of selected compounds at different matrices

Reaction matrix	Thioanisole		Fenthion		DBT	
	k (min^{-1})	$t_{1/2}$ (min)	k (min^{-1})	$t_{1/2}$ (min)	k (min^{-1})	$t_{1/2}$ (min)
High $\cdot CO_3^-$	2.02×10^{-2}	34.4	3.84×10^{-2}	18.0	2.80×10^{-2}	24.8
Bicarbonate radical	9.46×10^{-3}	73.2	2.76×10^{-2}	25.1	2.76×10^{-3}	251
Synthetic field water	9.18×10^{-3}	75.5	2.26×10^{-2}	30.7	2.60×10^{-3}	267
DOC + bicarbonate	6.84×10^{-3}	101	1.95×10^{-2}	35.5	1.92×10^{-3}	361
DOC + nitrate	9.23×10^{-3}	75.1	2.22×10^{-2}	31.2	2.71×10^{-3}	256
Filtered field water	8.08×10^{-3}	85.8	2.63×10^{-2}	26.3	2.47×10^{-3}	281
DI water	7.15×10^{-3}	96.9	2.48×10^{-2}	27.9	1.98×10^{-3}	350

relatively high concentration of Na_2CO_3 (0.04 M) and H_2O_2 (1.5 mM) owing to the higher production of hydroxyl and thus higher $\cdot CO_3^-$ produced via the scavenging by carbonate (Chen and Hoffman, 1974). The rate constants ranged from 7.15×10^{-3} min^{-1} in DI water to 2.02×10^{-2} min^{-1} in a high $\cdot CO_3^-$ matrix, which correspond to half-lives of 96.9 and 34.4 min, respectively. More importantly the degradation rates under realistic $\cdot CO_3^-$ concentrations were faster than direct photolysis (Fig. 4). In the filtered Lake Huron water at pH 8.1, the concentration of nitrate and bicarbonate was 6.2 and 105 ppm, respectively, while the amount of DOC was about 2.5 mg/l. These values were lower than in SFW, especially the amount of nitrate ion. The SFW and Lake Huron water yielded half-lives of 75.5 and 85.8 min, respectively. Enhanced degradation in these solutions suggests that the $\cdot CO_3^-$ could contribute to the cleansing of this compound from sunlit natural waters. Photolysis in the solution containing only DOC/bicarbonate was similar (half-life = 101 min) to direct photolysis in DI water. The rate in DOC/nitrate was the same as in SFW, indicating an increased $\cdot OH$ availability for reaction with thioanisole and reduced bicarbonate scavenging.

Fenthion and DBT show similar reactivities in different matrices (Table 2). The most rapid photoreaction was in the sodium carbonate with hydrogen peroxide matrix, followed by the sodium bicarbonate with nitrate ion matrix. The slowest photoreaction occurred in the matrix of DOC with sodium bicarbonate. The photolysis rate constants for fenthion were higher than thioanisole and ranged from 2.48×10^{-2} min^{-1} in DI water to 3.84×10^{-2} min^{-1} in a high $\cdot CO_3^-$ matrix; corresponding to half-lives from 27.9 to 18.0 min, respectively. Due to the relatively high direct photolysis rate in DI water for fenthion, the differences in rate constants between various matrices were small. The direct photolysis rate (half-life = 27.9 min) of fenthion was even slightly higher than the rate in SFW (half-life = 30.7 min) and in the DOC

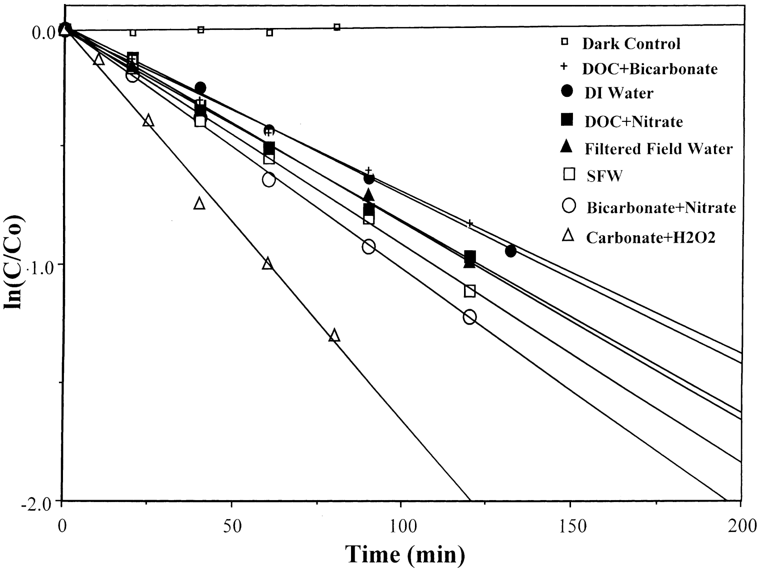


Fig. 4. Photoreaction kinetics of thioanisole under different reaction matrices.

plus nitrate matrix (half-life = 31.2 min), while the slowest rate (half-life = 35.5 min) was in the DOC/bicarbonate ion matrix. Photodegradation of fenthion in three matrices containing DOC all showed slower photolysis than under direct photolysis. These results suggest DOC's primary role in fenthion photolysis was to reduce the overall light intensity available for production of aqueous reagents and also to reduce the inherent direct photolysis pathway (Torrents et al., 1997). The filtered Lake Huron water and the bicarbonate radical solution yielded rate constants marginally faster than direct photolysis (26.3 and 25.1 min half-lives, respectively). In comparison to direct photolysis, the hydrolysis rate constant of fenthion at 25°C was 8.7×10^{-6} min^{-1} at pH 9 (Huang and Mabury, 1999), which is much slower than that for the photolysis rate observed here; similar conclusions for fenthion sulfoxide hold since the hydrolysis rate is 1.4×10^{-5} min^{-1} at pH 9. Therefore, photolysis of fenthion should contribute significantly to its primary degradation in sunlit field waters. The role of indirect photolysis via $\cdot CO_3^-$ reaction would be small.

DBT had a high photolysis rate constant of 2.80×10^{-2} min^{-1} in the high $\cdot CO_3^-$ matrix (half-life of 24.8 min), which was much higher than the direct photolysis rate constant of 1.98×10^{-3} min^{-1} in DI water (half-life of 350 min) (Table 2). The rate constant in the high carbonate matrix was also much higher than the rate constant in the bicarbonate matrix (2.76×10^{-3} min^{-1}), which indicated that the higher steady-state concentration of $\cdot CO_3^-$ formed in the system could enhance the photolysis rate dramatically. The lowest rate constant for DBT of 1.92×10^{-3} min^{-1} was found in the DOC and bicarbonate ion matrix as well. However, the measured half-life value of DBT in DI photolysis was much faster than the reference value (94 h) reported by Mill et al. (1981), presumably due to different wavelength and light intensities.

In general, the absorption of DOC gradually decreases with increasing wavelength, with essentially no absorption occurring above 550 nm. Most of the solar energy absorbed by DOC is between 300 and 500 nm. As the concentration of DOC increases, the integrated absorption also increases. As a result, DOC could shield the light intensity to lower the photolysis rate for the tested compounds and provide some indication that secondary DOC radicals (alkyl peroxy radicals) are not contributing much if any to the indirect photolysis pathway.

3.4. Photodegradation products

The primary photodegradation product for thioanisole in the different matrices was methyl phenyl sulfoxide. Approximately 30% of the thioanisole was converted to methyl phenyl sulfoxide in the high $\cdot CO_3^-$ matrix, while only 6% thioanisole was in DI water. Methyl phenyl sulfoxide was relatively stable in DI for the duration of these experiments (>2 h). No methyl phenyl sulfone was detected as a degradation product of thioanisole in different matrices due to the lower reactivity of methyl phenyl sulfoxide toward the $\cdot CO_3^-$ (Huang and Mabury, 2000).

The primary photodegradation product for fenthion was fenthion sulfoxide and 3-methyl 4-methylthiophenol. In addition to direct oxidation on the sulfur atom, as observed with thioanisole, direct photolysis breaking of the P–O bond to form the 3-methyl 4-methylthiophenol also occurred; as indicated above, hydrolysis would be too slow to yield the amount of phenol observed. Both mechanisms could have contributed to a more rapid photolysis of fenthion in comparison with thioanisole. Moreover, no fenthion sulfone was detected as a degradation product, presumably for similar reasons as for thioanisole.

Contrary to our expectations, DBT-sulfoxide was not observed as a degradation product in the photolysis of DBT in the SFW and related solutions. Under direct photolysis in DI water, DBT-sulfoxide degraded faster, with a rate constant of 5.0×10^{-2} min^{-1} in comparison with DBT with a rate constant of 2.0×10^{-3} min^{-1}. Approximately 5% of the DBT-sulfoxide was converted into DBT. It was also reported that photolysis of DBT-sulfoxide in organic solvents resulted in the formation of DBT and oxidized solvent (Gregory et al., 1997). These two observations may explain why a sufficient amount of DBT-sulfoxide was not found in the DBT photolysis. Furthermore, no DBT-sulfone was detected which may indicate its rapid photolysis or an alternate pathway of DBT-sulfoxide degradation. In contrast, the "high $\cdot CO_3^-$" solution did yield small amounts of DBT-sulfoxide but these were observed only after concentrating the sample.

4. Conclusions

The primary reaction pathways of the selected sulfur-containing compounds with $\cdot CO_3^-$ were through the sulfoxide, followed by the corresponding sulfone products. Three selected compounds were investigated under a photoreactor in different reaction matrices. Among all matrices, the most rapid photodegradation occurred in a carbonate radical matrix and bicarbonate radical matrix in comparison with direct photolysis. Because of the relatively high photodegradation rate in deionized water, the contribution of indirect photolysis through $\cdot CO_3^-$ was of intermediate importance.

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