Decomposition of hydrolysates of chemical warfare agents using photoactivated periodate

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Abstract

The kinetics and mechanism of periodate and photoactivated periodate oxidation of the hydrolysates of chemical warfare agents (HCWAs), thiodiglycol (TDG), 3,3-dithiopropanol (TDP), and 1,4-thioxane (TX), were investigated at pH 3, pH 7, and pH 10 under dark (in the absence of light) and monochromatic UV light irradiation. Dark reactions occurred by oxygen addition to sulfur atoms in HCWAs at pH 3 and pH 7 following the trend: TDP > TX > TDG. At pH 10 in the absence of light, both Malaprade and oxygen addition reaction mechanisms occurred in the reaction of $H_3IO_6^{2-}$ with HCWAs but at slower reaction rates compared to low pH dark reactions following the order: TDG > TDP > TX. The presence of monochromatic UV light at 220 nm, 240 nm, or 254 nm had insignificant improvements on HCWA degradation at low pH. At pH 10, the presence of 220 nm light resulted in an increase in degradation of HCWAs compared to dark reactions following the trend of electron density on the sulfur atom of the compound (TDP > TDG > TX). However, TDG, the compound with the largest dark reaction rate constant at pH 10 had the smallest percent increase in degradation due to the addition of light. Conversely, TX had the smallest dark reaction rate constant and the largest percent increase in degradation due to the addition of light. In the presence of light, the addition of t-butanol decreased degradation rates at pH 10 suggesting that $OH^\bullet$ plays an important role in the reactions. Degradation trends and kinetic modeling also suggest that iodyl radicals are involved in TX reactions.
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1. Introduction

The evolution of military technologies, along with ethical concerns, has resulted in chemical weapons being made redundant [1–3]. The United States has had a 30,600 tonnes stockpile of chemical warfare agents (CWAs) [1] and Russia has 40,000 tonnes of CWAs [2]. The baseline technology for destruction of CWAs is incineration; however, this is undesirable and often opposed by local communities due to perceived risks to the surrounding community [1]. Thus, alternative technologies are being explored [1]. Among the numerous alternative technologies explored [1,3], neutralization shows promise to treat CWAs, especially mustard agents (HD). Under low-temperature and low-pressure conditions, HD is hydrolyzed and the main hydrolysis product, thiodiglycol (TDG), is much less toxic [1].

However, treatment of TDG by another means is necessary to further degrade this hydrolysis product of the CWA (HCWA).

In aqueous solution, periodic acid is a strong oxidant and forms a variety of species depending on pH, concentration, and the presence of other components in solution [4–7]. In acidic solution the predominant species is the tetrahedral IO_4^- anion due to dehydration of the monoanion, $H_4IO_6^-$. In dilute alkaline solution, the dominant monomeric periodate ions are the octahedral $H_3IO_6^{2-}$ anion and $H_2IO_6^{3-}$ [4]. The standard reduction potential for the periodate–iodate couple in acidic solution is approximately +1.6 V; in alkaline solution, the value is reduced to +0.7 V [7]. Periodate has been used as a selective oxidant for compounds such as 1,2-diols, 1,2-ketonealdehydes, 1,2-diketones, 1,2-hydroxyaldehydes, and 1,2-aminoalcohols [6]. The typical reaction pathway, called a Malaprade reaction, includes the formation of a cyclic intermediate. The rate of reaction is dependent on pH and steric effects with the relative stability of the intermediate complex playing a key role [6]. Periodate also reacts with sulfur

Table 1
Proposed periodate photolysis reactions in the pH range 2.44–4.90 [11]

Reaction step	Reaction		Reaction rate constant
Initiation	$IO_4^- + h\nu \rightarrow IO_4^{-*}$	(1)	
	$IO_4^{-*} + h\nu \rightarrow IO_3^{\bullet} + O^{\bullet -}$	(2a)	
	$IO_4^{-*} + h\nu \rightarrow IO_3^- + O(^3P)$	(2b)	
	$IO_4^{-*} + h\nu \rightarrow IO_3^- + O(^1D)$	(2c)	
Propagation	$O^{\bullet -} + H^+ \leftrightarrow OH^{\bullet}$	(3)	
	$OH^{\bullet} + IO_4^- \rightarrow OH^- + IO_4^{\bullet}$	(4a)	$k_{(4a)} = 4.5 \times 10^8 \, M^{-1} \, s^{-1a}$
	$OH^{\bullet} + IO_3^- \rightarrow OH^- + IO_3^{\bullet}$	(4b)	$k_{(4b)} = 1.7 \times 10^7 \, M^{-1} \, s^{-1a}$
	$O_3 + IO_3^{\bullet} \rightarrow IO_4^{\bullet} + O_2$	(5)	
Termination	$2OH^{\bullet} \rightarrow H_2O_2$	(6)	$k_{(6)} = 6 \times 10^9 \, M^{-1} \, s^{-1a}$
	$2IO_4^{\bullet} \leftrightarrow I_2O_8$	(7)	
	$I_2O_8 + H_2O \rightarrow IO_3^- + IO_4^- + 2H^+ + O_2$	(8)	$k_{(8)} = 1.5 \times 10^8 \, M^{-1} \, s^{-1a}$
	$2IO_3^{\bullet} \leftrightarrow I_2O_6$	(9)	$k_{(9)} = 4 \times 10^8 \, M^{-1} \, s^{-1a}$
	$I_2O_6 + H_2O \rightarrow IO_3^- + IO_4^- + 2H^+$	(10)	$k_{(10)} = 4.5 \times 10^8 \, M^{-1} \, s^{-2a}$
	$O_2 + O(^3P) \rightarrow O_3$	(11)	
	$O(^3P) + O(^3P) \rightarrow O_2$	(12a)	
	$O_3 + O(^3P) \rightarrow 2O_2$	(12b)	
	$O(^1D) + H_2O \rightarrow H_2O_2$	(13)	

[a] Reaction rate constant calculated in Ref. [29].

containing compounds as an electrophilic oxidant transferring oxygen to the organic sulfide atom. Hydroxylalkyl sulfides react with periodate in the absence of light via two possible pathways: one is Malaprade reactions to break carbon–carbon bonds at α-hydroxyl β-thiosulfide or γ-thiosulfide groups forming formaldehyde, and the other is oxygen addition to the sulfur atom [5–7].

Upon UV irradiation, periodate is photoactivated producing a series of reactive intermediates over a wide range of pH [8–13]. Among the numerous proposed mechanisms for photoactivated periodate, the mechanism suggested by Wagner and Strehlow is broadly cited [11]. Reactive intermediates, namely $OH^{\bullet}$, $IO_4^{\bullet}$, $IO_3^{\bullet}$, $O(^3P)$, $O(^1D)$ and O_3, are generated that are susceptible to react with organics as shown in Table 1. In addition, possible regeneration of IO_4^- by $IO_4^{\bullet}$ and $IO_3^{\bullet}$ radicals is indicated in this reaction mechanism as shown in Eqs. (7)–(10). $IO_3^{\bullet}$ and $IO_4^{\bullet}$ are suggested to be the dominant iodine intermediates formed during the photolysis of IO_4^- [11]. These iodine radicals are believed to play key roles in the photo-assisted degradation of organic substrates, especially in the presence of hydroxyl radical scavengers [8]. Under alkaline conditions the reactive iodine species have only been characterized as periodyl (I^{VIII}) and iodyl (I^{VI}) radicals [9,10].

Multiple radical based advanced oxidation processes (AOPs) show advantages over other AOP techniques based only on hydroxyl radical scavengers [8,14–15]. Photoactivated periodate is one such AOP. For example, photoactivated periodate has been shown to decompose a matrix of industrial wastewater with high concentrations of triethanolamine and high chemical oxygen demand faster than other AOPs investigated [13]. Previous work in this laboratory demonstrated that $IO_3^{\bullet}$, $IO_4^{\bullet}$, and $O(^3P)$ were important species responsible for 4-chlorophenol degradation in the photoactivated periodate system at pH 3 with a monochromatic light source [8]. A minor decrease in the degradation rate was observed in the presence of high concentrations of an $OH^{\bullet}$ scavenger, t-butanol.
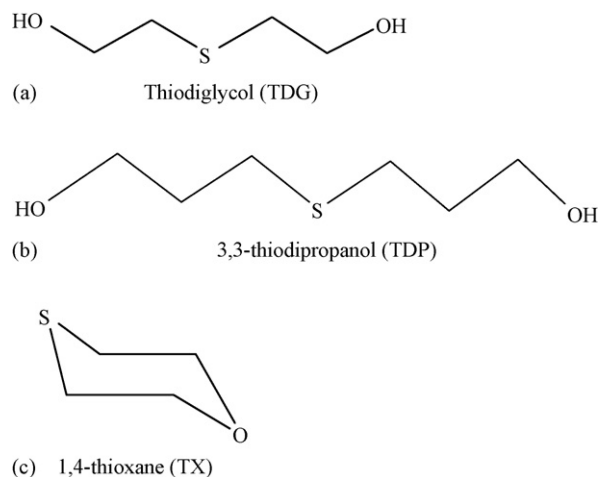

Fig. 1. Chemical structure of TDG (a), TDP (b), and TX (c).

The objective of this study was to investigate the kinetics and mechanism of photoactivated periodate oxidation of HCWAs of HD, specifically: TDG; a similar compound with larger carbon chain length, 3,3-dithiopropanol (TDP); and a compound with a cyclic structure, 1,4-thioxane (TX), as shown in Fig. 1 [16]. TDG, TDP, and TX were chosen as model hydroxylalkyl sulfides to provide reaction information on carbon chain length and steric effects. Effects of periodate speciation, wavelength of light and presence of an $OH^{\bullet}$ radical scavenger were determined. By monitoring HCWAs, IO_4^-, IO_3^-, and O_3, evidence of photoactivated periodate reaction pathways were observed.

2. Experimental

2.1. Materials

All major chemicals used were of reagent grade or higher except where further description is given. Periodic acid (Fisher

Scientific), sodium iodate (Fisher Scientific), lithium hydroxide (Acros), perchloric acid (Fisher Scientific), thiodiglycol (Sigma–Aldrich), 3,3-thiodipropanol (Sigma–Aldrich), 1,4-thioxane (Sigma–Aldrich), *tert*-butanol (*t*-BuOH, Fisher Scientific), purpald (Aldrich), sodium boro-hydrate (Fisher Scientific), and 37% formaldehyde stabilized solution (Fisher Scientific) were used as received. Thiodiglycol sulfoxide (TDGO) from Chem Service Inc. was analyzed by NMR showing two similar compounds with properties present in approximately the same ratio. It is very likely that the two compounds in TDGO are the interconversion isomers of TDGO. Water used in experiments was from a Milli-Q system (Milli-RX45, Milli-pore) with a resistance of 18.2 MΩ cm.

2.2. Reactor

All experiments were conducted inside a black-painted wooden box (0.8 m × 1.2 m × 1.1 m) to avoid any potential reactions with laboratory fluorescent light. Reactions were carried out in a horizontally placed 500 mL water-jacketed glass cylindrical reactor with a quartz window and six vertical ports on top as shown in Fig. 2. These ports functioned as a sampling location, a Tedlar gas bag inlet, dissolved oxygen probe (Orion 810) inlet, Sure-flow Ross semi-micro pH electrode (ThermoOrion) inlet, autotitrator of a pH-stat controller (PHM 290, Radiometer/Copenhagen) inlet, and the final port was sealed [8]. A water-cooling system (ISOTEMP 1006S, Fisher Scientific) was used to maintain the temperature of solution inside the reactor at 20 ± 0.5 °C. The distance between the irradiated surface and the output from the water filter was approximately 49 mm. For dark reactions, periodate was adjusted to the desired concentration and pH. Then, HCWA was injected to the reaction system at $t = 0$. For UV light reactions, the light was shielded from the reactor prior to the start of irradiations. At $t = 0$ HCWA was injected into the reactor under the same conditions as the dark reactions except at $t = 0$ the light shield was removed.
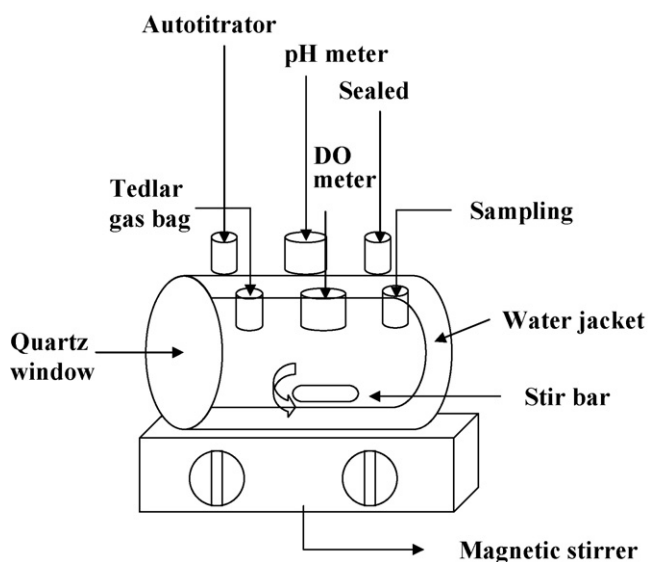

Fig. 2. Schematic diagram of the photochemical reactor.

2.3. Light source

The light source for all light experiments was a 500 W Hg(Xe) arc lamp (Oriel 66142) with a built in ignitor (Oriel 66028) and switched-mode arc lamp power supply (Oriel 68811). In order to diminish the heating effect of IR irradiation, a water filter was applied just after the lamp housing in all experiments. Light experiments at $\lambda = 240$ nm and $\lambda = 254$ nm used a monochromator (Oriel 74000) and were conducted following procedures of Chia et al. [8]. Light experiments using an optical filter (Oriel 58560, 2 in. diameter) provided light at 220 ± 5 nm. The power output was measured by a UV silicon probe (Oriel 70282) equipped with a radiant power meter (Oriel 70260). Prior to all light experiments the Hg(Xe) lamp was balanced for at least 1 h.

2.4. Reaction conditions

Stock solutions of 0.25 M periodic acid, 0.25 M TDG, 0.1 M TDP, and 0.1 M TX were prepared and stored at 4 °C covered with aluminum foil to prevent light reactions. About 500 mL of the appropriate concentration of periodic acid was prepared from the stock solution in each experiment. Due to the low solubility of sodium periodate at high pH, a fresh filtered 5N LiOH solution was applied to adjust the initial pH (pH 3, pH 7 or pH 10) of the reaction system. Otherwise 1N LiOH or 1.5N HClO$_4$ was loaded in the pH-stat system (PHM 290, Radiometer) to maintain the pH during reactions. For experiments with *t*-BuOH, pure *t*-BuOH was added to periodate solutions to achieve a final concentration of 120 mM. A Chemware Tedlar gas bag of air was connected to the photochemical reactor through a valve to keep the experimental system isobaric during all experiments. Prior to photolysis, 10 mL of sample was withdrawn for analysis of periodate and iodate, formaldehyde, and O$_3$. Next, a proper quantity of HCWA stock solution was injected into the photochemical reactor to have a reaction volume ranging from 492–495 mL. Due to the large amount of sample required for analysis, two sets of experiments were conducted for each kinetic run in order to keep changes in the volume of the reaction system to within 15% during the course of the reaction. Selected experiments were run in duplicate to ensure reproducibility.

2.5. Sampling

About 6–8 mL samples were withdrawn at selected time intervals and placed in amber glass vials. Except for ozone measurements, samples were purged with nitrogen gas (99.999% purity) through a stainless steel needle for 5 min to remove residual ozone. For HCWA and HCWA sulfoxide (HCWAO) analysis, 2 mL samples were added to 4 mL of 0.05 M barium hydroxide solution to quench residual periodate. A 0.45 μm PVDF filter (Whatman, 6872-1304) to remove insoluble barium salts was connected to a pre-wetted IC-H cartridge (Alltech 30264). The IC-H cartridge was used to exchange cations with protons and to avoid the formation of barium carbonate precipitates formed from excess barium ion in solution contacting CO$_2$ from ambi-

ent air. Formaldehydes were observed to be concentrated during the process of ion exchange by IC-H cartridges [17]. Therefore, formaldehyde, along with periodate, iodate, ozone, and sulfur containing compounds, were quantified without any sample pre-treatment.

2.6. Analytical procedures

Periodate and iodate were analyzed by a HP³ᴰ Capillary Electrophoresis system (Agilent) coupled to a diode array detector with a standard bare fused silica capillary (40 cm long × 50 μm i.d., G1600-60132) and detected at 200 nm for iodate and 220 nm for periodate [8,18]. An acetate buffer at pH 4.45 and concentration of 100 mM was used as a carrier and replenishing buffer. A 50 mbar injection pressure and −25 kV applied voltage was used; the temperature of the capillary was maintained at 30 °C.

Analysis of TDG, TDP, and TX were carried out by HPLC (Agilent, Series 1100) on an Agilent SB C_{18} column (2.1 mm × 150 mm, with 5 μm particle size). The detection wavelength was 210 nm for all HCWAs. An eluent flowrate of 0.2 mL min⁻¹ of 95% phosphate buffer (H_3PO_4/Na_2HPO_4) at pH 2.2 and 5% acetonitrile, and injection volume of 2 μL at 25 °C was applied for this isocratic analysis. Samples were injected three times and the chromatographic results were the average value of the second and the third injection. Control experiments showed no significant difference in the results using either three or five injections.

Thiodiglycol sulfoxides were detected by electron spray ionization mass spectrometry (ESI-MS) (Esquire-LC, Bruker) and verified by ESI-MS–MS under positive ionization mode [19–21]. The method used a solvent mixture with 50:50 water and methanol at a flow rate of 0.2 mL min⁻¹ under cone voltage of 50 V. An internal standard (TDG) was used for quantitation purposes.

Formaldehyde was determined by sample derivatization with 4-amino-5-thioxo-3-hydrazine-1,2,4-triazdidine-3-one (4-amino-5-hydrazine-3-mercapto-1,2,4-trizone, AHMT) and detected by spectrophotometry [22]. Briefly, 0.1 mL formaldehyde solution diluted to 1 mL was derivatized with 1.5 mL 1% AHMT for 30 min on a rotary shaker at 200 rpm. About 2.5 mL 0.2% $NaBH_4$ in 1N NaOH was then mixed with the solution and followed by UV–vis spectrometry (UV-2401 PC, Schimadzu) at 550 nm. Both AHMT and $NaBH_4$ solutions were prepared immediately before each experiment.
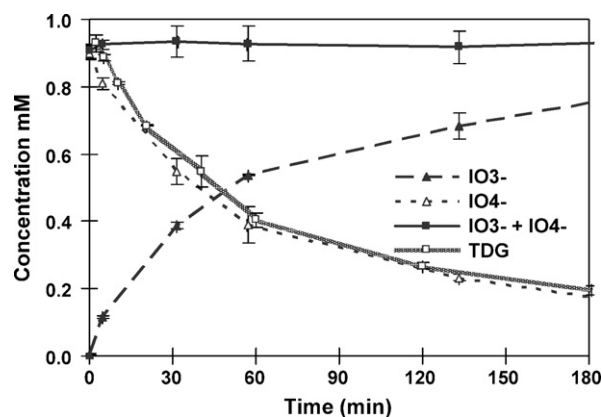

Fig. 3. Reactions of 1 mM periodate with 1 mM TDG at pH 3 under dark conditions.

Aqueous O_3 was determined using the indigo method [23].

3. Results and discussion

3.1. Dark reactions

To determine the kinetics and mechanism of periodate with HCWAs in the absence of light, initial experiments were conducted without UV irradiation. As shown in Fig. 3, reaction between periodate and TDG occurred rapidly at pH 3. Periodate was consumed forming a stoichiometric amount of iodate. TDG degraded at a similar rate to periodate. Dark reactions were observed to follow second-order kinetics. However, dark reactions that were used to compare to light systems were conducted with an [IO_4^-]:[HCWA] ratio of 5:1; therefore, degradation of HCWAs were found to follow pseudo first-order kinetics with respect to [HCWAs] as shown in Table 2 (k_{dark}). TDG sulfoxide (TDGO, $m/z = 139$) was observed as the primary organic reaction product by ESI-MS–MS spectra matching of the product and a TDGO standard. In addition, no formaldehyde was detected. Dark reactions of TDP and TX with periodate were similar to the reaction of TDG with periodate. TDP sulfoxide (TDPO, $m/z = 167$) and TX sulfoxide (TXO, $m/z = 121$) were observed as the primary reaction products by ESI-MS and ESI-MS–MS. The lack of formaldehyde and the formation of sulfoxides at pH 3 indicates that the reactions followed the oxygen addition pathway rather than a Malaprade reaction pathway [24].

Table 2
Pseudo first-order reaction rate constants of 1 mM HCWAs by [IO_4^-]$_0$ = 5 mM under dark, 220 nm UV, and 220 nm UV in the presence of t-BuOH at pH 3 and pH 10

	pH 3[a]		pH 10[a]					
	$k_{overall}$	k_{dark}	$k_{overall}$	k_{dark}	$k_{UV/H_3IO_6^{2-}}$	$k_{t\text{-BuOH}}$	k_{OH}	k_{other}
TDG	18	16 ± 2	3.7	1.2	2.5	1.3	2.5	0.04
TDP	ND	63 ± 2	4.7	1.1	3.6	1.4	3.2	0.36
TX	ND	23 ± 2	2.4	0.4	2.0	0.98	1.4	0.58

ND, not determined.
[a] Reaction conditions: k (×10⁻⁴ s⁻¹); λ = 220 nm; E = 80.6 μW cm⁻².

Oxidation of HCWAs by periodate at pH 3 followed the trend: TDP > TX > TDG. Reaction via oxygen addition to the sulfur atom would predict a reaction trend based on electron density on the sulfur atom (TDP > TDG > TX). Control experiments showed no reaction between iodate and TDG, TDP, or TX at pH 3. In addition, there was no detectable reaction between periodate and TDGO. Compared to TDG, the longer carbon chain length of TDP provides more electron density to the sulfur atom. Therefore, TDP had a higher degradation rate than TDG. TX has a slightly lower electron density on the sulfur atom of TX than TDG. However, the cyclic structure of TX better exposed the sulfur atom in the molecule to oxidation compared to TDG. Thus, despite its lower electron density on the sulfur atom, TX had a faster degradation rate than TDG. Therefore, overall, both electron density on the sulfur atom in HCWAs and steric effects played a role at pH 3.

At pH 7, the dark reaction proceeded similarly to pH 3 (data not shown). Both the order and rate constants of reaction for TDG, TDP, and TX were the same at pH 3 and pH 7. Moreover, the formation of HCWAOs and the absence of formaldehydes were similar at both pH values. This result is expected because the speciation of periodate and HCWAs do not change between these pH values.

At pH 10, HCWA species remained unchanged. However, kinetic data showed different results from pH 3 and pH 7 (Table 2) due to a change in the dominant periodate species in water from IO_4^- to $H_3IO_6^{2-}$ under our experimental conditions [25]. Under this high pH, both HCWAO and formaldehyde were detected. Reaction rates of HCWAs in the dark periodate system at pH 10 followed that expected from a Malaprade reaction pathway: TDG > TDP > TX (Table 2). The change in selectivity of degradation of HCWAs by periodate and the presence of formaldehyde as a product of reaction suggests a change in the reaction pathway. The formation of formaldehyde suggests that reactions occur, at least partially, through a Malaprade pathway. Moreover, periodate oxidized HCWAs rapidly at pH 3 and pH 7, whereas at pH 10 reactions occurred at a slower rate although both oxygen addition and Malaprade reaction pathways occurred.

These results suggest pH affects reaction by both mechanisms. First, the decreased rate of oxygen addition to HCWAs by periodate at high pH may due to the larger size of $H_3IO_6^{2-}$ compared with IO_4^- making it more difficult to attack the sulfur atom in HCWAs. The lower rate at high pH is also consistent with a decreased reduction potential of periodate at high pH (decreased from +1.6 to +0.7 V). Second, Malaprade reactions produce a rate-limiting cyclic intermediate that can be acid or base catalyzed [6]. Reaction of HCWAs via the Malaprade pathway appears to be much slower compared to oxygen addition to the sulfur atom reaction even at the optimal high pH condition based on our experimental results. Furthermore, the sharp decline in the degradation rate of TX at high pH is consistent with the structure of TX [24]. The energy to break down the periodate *trans*-diol intermediates by the Malaprade pathway is elevated enormously compared to *cis*-diols; thus, the *cis*-diols (TDG and TDP) were oxidized much faster than the *trans*-diol compound (TX) consistent with the Malaprade pathway [6].
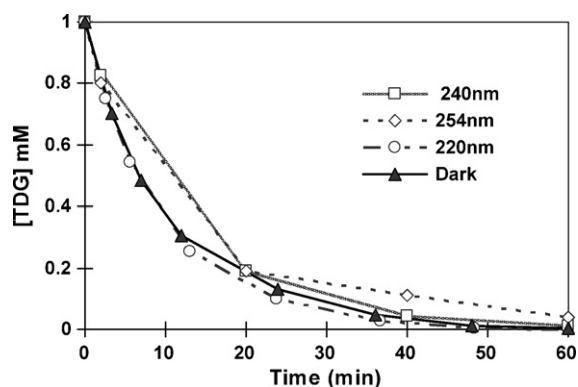

Fig. 4. TDG degradation by $[IO_4^-]_0 = 5$ mM with and without monochromatic UV light at pH 3 ($E_{\lambda=220nm} = 80.6\,\mu W\,cm^{-2}$; $E_{\lambda=240nm} = 9.6\,\mu W\,cm^{-2}$; $E_{\lambda=254nm} = 11.2\,\mu W\,cm^{-2}$).

3.2. Irradiation at pH 3

Extinction coefficients of compounds of interest were investigated by UV–vis spectrophotometry (data not shown). All ε_{HCWA}s were substantially lower than the extinction coefficient of I^{VII}, ε_{Ivii}. A screening factor [25,26] indicated nearly complete light attenuation by IO_4^- on the direct photolysis rate. With the existence of periodate, HCWAs are minor species absorbing UV output resulting in less than 0.01% of HCWA loss by direct photolysis. Thus, direct photolysis of HCWAs was negligible. At pH 3, irradiations were conducted at three wavelengths: 254 nm (11.2 $\mu W\,cm^{-2}$), a commonly used wavelength in photochemical research; 220 nm (80.6 $\mu W\,cm^{-2}$), a wavelength close to the maximum extinction coefficient of periodate (222 nm), and 240 nm (9.6 $\mu W\,cm^{-2}$) for comparison purposes.

Surprisingly, no difference in the degradation rate of TDG was observed under any of these irradiation conditions compared to dark reactions, even at the highest light intensity of 80.6 $\mu W\,cm^{-2}$ at λ_{max} 220 nm as shown in Fig. 4. Under monochromatic UV irradiation and in an excess of periodate, organics reacted with periodate following pseudo first-order reaction kinetics [8,12,27] as shown in the following equation:

$$\frac{d[HCWA]_0}{dt} = -k_{overall}[HCWA] \qquad (14)$$

where $d[HCWA]_0/dt$ is the initial HCWA degradation rate and $k_{overall}$ is the overall pseudo first-order degradation rate constant observed due to light and dark reactions. To confirm that the addition of UV to the dark periodate system was negligible under our conditions, Eq. (14) was separated into dark and light reaction components:

$$\frac{d[HCWA]_0}{dt} = -k_{overall}[HCWA]$$
$$= -k_{dark}[HCWA] - k_{UV/IO_4^-}[HCWA] \qquad (15)$$

and

$$k_{overall} = k_{dark} + k_{UV/IO_4^-} \qquad (16)$$

where k_{dark} is the pseudo first-order degradation rate constant of HCWA observed over the initial degradation period in the dark

Table 3
Percentage of pathway contribution to HCWA degradation

pH	HCWA	% of pathway contribution to HCWA degradation			
		Dark[a]	Light $\lambda = 220\,nm$[b]		
			Total	OH$^\bullet$ influenced	Other radicals
3	TDG	93 ± 12	7 ± 12	ND[c]	ND[c]
10	TDG	33	67	66	1.1
	TDP	23	77	69	7.7
	TX	16	84	60	24

[a] Dark represents the measured dark reaction in the absence of light.
[b] Light represents the kinetic residual effect of adding 220 nm light.
[c] ND, not determined.

and k_{UV/IO_4^-} is the pseudo first-order degradation rate constant representing the residual kinetic effect due to light. It should be noted that the dark pathway will be reduced to some degree as a fraction of periodate is photolyzed, reducing the concentration of periodate reacting by the dark pathway. Thus, the kinetic equation representing the system would be:

$$k_{overall} = k'_{dark} + k'_{UV/IO_4^-} \qquad (17)$$

where k'_{dark} is the altered pseudo first-order degradation rate constant when light reactions are present ($k'_{dark} \leq k_{dark}$) and k'_{UV/IO_4^-} is the true pseudo first-order degradation rate constant ($k'_{UV/IO_4^-} \geq k_{UV/IO_4^-}$). However, it is impossible to determine the values of k'_{dark} and k'_{UV/IO_4^-} from the experiments performed. For our purposes, we were interested in evaluating and characterizing conditions where photoactivated periodate was beneficial over dark reactions of periodate; thus, we report our results in terms of k_{dark} and k_{UV/IO_4^-}, the kinetic residual effect of adding light. The small value for k_{UV/IO_4^-} ($2 \pm 2 \times 10^{-4}\,s^{-1}$) compared to k_{dark} ($16 \pm 2 \times 10^{-4}\,s^{-1}$) for TDG at pH 3 confirms that the degradation of TDG by photoactivated periodate was not accelerated compared to dark reactions. As shown in Table 3, the light pathway contribution to the degradation of TDG at pH 3 is within the error of the experiments.

In the presence of light, periodate itself as well as radicals generated from periodate photolysis are expected to react with TDG. These two parallel pathways compete with each other. In the UV/IO$_4^-$/TDG system at low pH, direct reaction between periodate and TDG appears to be the dominant pathway for TDG degradation because no apparent improvement was observed upon the addition of light. Thus, radicals played minor roles and had negligible effects. Although radicals often react with organics at diffusion limited rates, the negligible improvement with light reflects the relatively small amount of radicals generated reacting with TDG at fast rates compared to the relatively large amount of periodate reacting with TDG at moderate rates. Among the three HCWAs, reaction between TDG and periodate had the lowest rate at pH 3. Because no improvement was observed by the addition of light to the slowest reaction system, it is reasonable to predict that no improvement will occur with other HCWAs under the same conditions. Furthermore, no observable improvement was expected at pH 7 due to the same

speciation and dark reaction kinetics of periodate and HCWAs at both pH 3 and pH 7.

3.3. Irradiation at pH 10

At pH 10, experiments were carried out at 220 nm with an intensity output of 80.6 μW cm^{-2}. Compared to the other wavelengths investigated at pH 3, 220 nm had the most energetic and greatest number of photons entering the system. In addition, periodate has its highest extinction coefficient at 222 nm. Thus, this condition had the highest likelihood for improvement. As shown in Fig. 5, a remarkable improvement in the HCWA degradation rate was observed compared to dark reactions for all HCWAs tested. This result suggests that in addition to periodate itself, radicals generated from periodate during irradiation play important roles in HCWA oxidation at pH 10. In 5 mM periodate solutions, H$_3$IO$_6$$^{2-}$ is the dominant periodate species at pH 10 [25]. Under dark conditions the reactivity of HCWAs with H$_3$IO$_6$$^{2-}$ is over an order of magnitude slower than IO$_4^-$. The slower reaction rate under dark conditions at pH 10 allows small concentrations of radicals formed by photolysis of periodate to influence the overall degradation rate at pH 10. Thus, remarkable improvements were monitored.

To determine the impact of adding light to the system, the fraction of HCWAs reacting by light and dark processes were quantified based on Eqs. (18) and (19):

$$\frac{d[HCWA]_0}{dt} = -k_{overall}[HCWA]$$
$$= -k_{dark}[HCWA] - k_{UV/H_3IO_6^{2-}}[HCWA] \qquad (18)$$

and

$$k_{overall} = k_{dark} + k_{UV/H_3IO_6^{2-}} \qquad (19)$$

where k_{dark} is the pseudo first-order degradation rate constant of HCWA in the dark at pH 10 observed over the initial degradation period and $k_{UV/H_3IO_6^{2-}}$ is the kinetic residual effect due to the addition of light at pH 10. As observed in Table 2 at pH 10, the overall degradation due to light and dark degradation is fastest for TDP followed by TDG and TX. This trend is consistent with electron density on the sulfur atom in the compounds. In addition, we observed that the dark component becomes a much smaller contribution to the overall degradation rate constant compared to pH 3. Table 3 shows that the dark
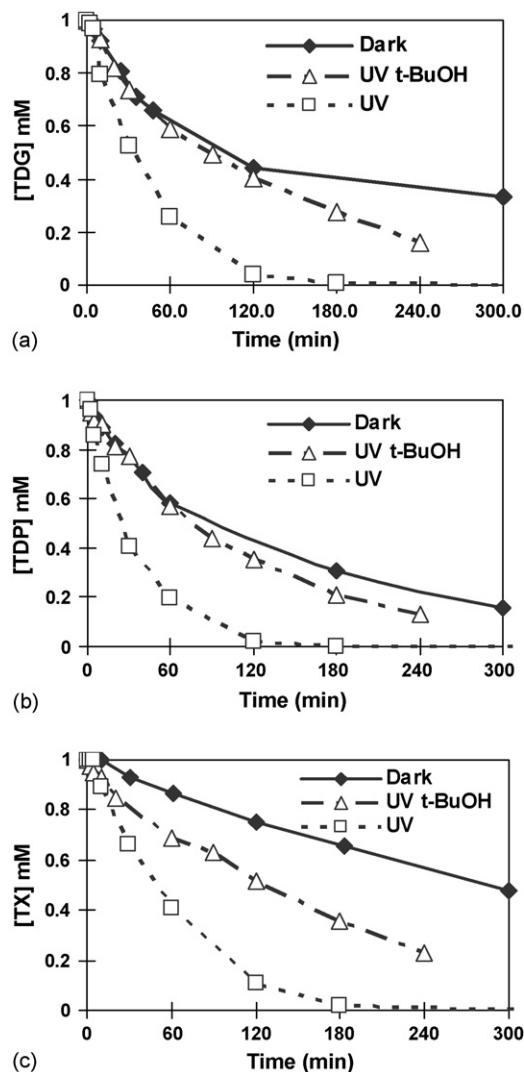
Fig. 5. HCWA degradation by $[H_3IO_6^{2-}]_0 = 5$ mM under dark, 220 nm UV, and 220 nm UV in the presence of 120 mM t-butanol at pH 10: (a) TDG; (b) TDP; (c) TX.

contributions for HCWA degradation are now minor compared to the combined presence of light and periodate. Moreover, the HCWA with the largest dark reaction rate constant (TDG) had the smallest percent increase due to the addition of light.

At pH 10 under 220 nm irradiation, $H_3IO_6^{2-}$ is photoactivated and radical and non-radical species such as $OH^{\bullet}$, I^{VIII}, I^{VI}, $O(^3P)$, and O_3 are possibly generated [10]. In order to investigate if $OH^{\bullet}$ was the dominant species responsible for degradation of HCWAs at pH 10, t-BuOH was added in excess to quench $OH^{\bullet}$ in the photoactivated periodate system. As seen from Fig. 5, degradation of HCWA is decreased significantly in the presence of t-BuOH compared to in the absence of t-BuOH under 220 nm irradiation. However, improvements were still observed compared to the dark reaction condition. To quantify the contribution of $OH^{\bullet}$ to the degradation of HCWAs at pH 10, the light components were separated into $OH^{\bullet}$ and other reactive species (e.g., $O(^3P)$, I^{VI}, O_3).

$$k_{UV/H_3IO_6{}^{2-}} = k_{overall} - k_{dark} = k_{OH^{\bullet}} + k_{other} \qquad (20)$$

where

$$k_{other} = k_{t\text{-BuOH}} - k_{dark} \qquad (21)$$

and

$$k_{OH^{\bullet}} = k_{overall} - k_{t\text{-BuOH}} \qquad (22)$$

k_{other} is the difference between the observed rate constant in the presence of t-BuOH under UV irradiation and the dark reaction; $k_{t\text{-BuOH}}$ is the pseudo first-order degradation rate constant of HCWAs at pH 10 in the presence of t-BuOH and 220 nm irradiation. In other words, $k_{t\text{-BuOH}}$ is the light reaction rate constant when the hydroxyl radicals were quenched by t-BuOH. And $k_{OH^{\bullet}}$ is the apparent pseudo first-order degradation rate constant of HCWAs by $OH^{\bullet}$. Note that when hydroxyl radical reacts with t-BuOH, it suppresses the reactions between $OH^{\bullet}$ and periodate and iodate ions. This will suppress the oxidation of HCWAs by hydroxyl radicals, iodyl radicals (resulting from Eqs. (4a) and (4b)) and periodyl radicals. However, I^{VI} formed from primary photolysis will not be affected by t-BuOH.

Table 3 shows that $OH^{\bullet}$ appears to be the major radical species reacting with HCWAs upon the addition of light. However for TX, other radical species also play an important role in degradation. In a previous study, $IO_3^{\bullet}$ and $O(^3P)$ were shown to play an important role in the degradation of 4-chlorophenol in the photoactivated periodate system at pH 3 [8]. $OH^{\bullet}$ played a minor role in the reaction system. Lee and Yoon determined that $OH^{\bullet}$ and $IO_3^{\bullet}$ were the main oxidants in the photoactivated periodate degradation of reactive black 5 dye in the pH range of 1.5–10 [27]. For HCWAs in our system at pH 10, degradation by an $OH^{\bullet}$ pathway ($k_{OH^{\bullet}}$) appears to be linked to the electron density on the S atom. No apparent steric effects were observed because the mechanism involves radical attack rather than forming a cyclic intermediate via a Malaprade pathway. In addition, the small size of $OH^{\bullet}$ minimizes the influence of steric effects. Thus, HCWAs with higher electron density on the sulfur atom had a larger light component reacting by an $OH^{\bullet}$ pathway. In addition, $k_{OH^{\bullet}}$ is the largest component of the light reaction pathway resulting in $k_{UV/H_3IO_6{}^{2-}}$ following the same degradation pathway trend as $k_{OH^{\bullet}}$.

Dissolved oxygen (DO) measurements (data not shown) demonstrate that oxygen is present and stable in $UV/H_3IO_6^{2-}$ systems with HCWAs. However, no O_3 was measured at pH 10. No measurable O_3 observed during reactions at pH 10, may be due to the rapid decomposition of O_3 in alkaline solution [28,29] rather than the lack of $O(^3P)$ to react with O_2 to form O_3. Therefore, although O_3 is not a plausible reactive species at pH 10, $O(^3P)$ is a possible reaction intermediate oxidizing HCWA at pH 10 in the presence of t-BuOH.

The relatively large value of k_{other} for TX suggests that k_{other} is influenced by steric factors. I^{VI} and $O(^3P)$ are reactive components attributed to k_{other} at pH 10. Similar to $OH^{\bullet}$, $O(^3P)$ is not expected to be influenced by steric factors but the larger size of I^{VI} is expected to be influenced by sterics. Thus, this indirect evidence suggests that I^{VI} may be an important reactant for TX but a minor player for TDG and TDP. Thus, it appears that the compound reacting in the photoactivated periodate system is an

important variable in determining the destruction pathway at a particular pH.

Therefore, an improvement of degradation rates of HCWAs at pH 10 demonstrates that $OH^\bullet$ and I^{VI} were generated and contributed to the degradation of HCWAs by photolysis. Hydroxyl radical does play an important role in the photoactivated periodate reaction system without the presence of *t*-BuOH. For TDG and TDP, $OH^\bullet$ is the dominant species for HCWA degradation. I^{VI} plays a minor role. However, for TX with its cyclic structure and lower electron density on the S atom, I^{VI} contributes significantly to its degradation. This demonstrates that I^{VI} is either more effective at oxidizing TX compared to TDG and TDP or $OH^\bullet$ reacts more slowly with TX compared to TDG and TDP.

4. Conclusions

The reaction mechanism of IO_4^- with HCWAs in the absence of light follows an oxygen addition pathway at pH 3 and pH 7. The same periodate speciation at pH 3 and pH 7 resulted in the same oxidation rate of HCWAs with IO_4^-. Both Malaprade and oxygen addition pathways were observed in the reaction of $H_3IO_6^{2-}$ with HCWAs at pH 10. Under 220 nm, 240 nm, or 254 nm UV irradiation, no significant improvement was observed with respect to degradation rates of HCWAs by IO_4^- at pH 3. However, improvement was observed at pH 10 with and without the presence of *t*-BuOH. Hydroxyl radicals appear to be the dominant species for oxidation of TDG and TDP in the UV system but another radical, likely I^{VI}, plays a large role in the degradation of TX. These results suggest that degradation by photoactivated periodate is faster for compounds with higher electron density on the sulfur atom and that the degradation pathway is compound specific.

Acknowledgements

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