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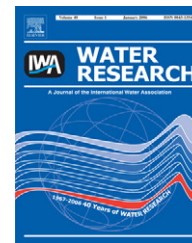*University of California - Los Angeles*, msuffet@ucla.edu

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Reactions of thiocarbamate, triazine and urea herbicides, RDX and benzenes on EPA Contaminant Candidate List with ozone and with hydroxyl radicals

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ABSTRACT

Second-order rate constants of the direct ozone reactions ($k_{O_3,M}$) and the indirect OH radical reactions ($k_{OH,M}$) for nine chemicals on the US EPA's Drinking Water Contaminant Candidate List (CCL) were studied during the ozonation and ozone/hydrogen peroxide advanced oxidation process (O_3/H_2O_2 AOP) using batch reactors. Except for the thiocarbamate herbicides (molinate and EPTC), all other CCL chemicals (linuron, diuron, prometon, RDX, 2,4-dinitrotoluene, 2,6-dinitrotoluene and nitrobenzene) show low reactivity toward ozone. The general magnitude of ozone reactivity of the CCL chemicals can be explained by their structures and the electrophilic nature of ozone reactions. The CCL chemicals (except RDX) are highly reactive toward OH radicals as demonstrated by their high $k_{OH,M}$ values. Ozonation at low pH, which involves mainly the direct ozone reaction, is only efficient for the removal of the thiocarbamates. Ozonation at high pH and O_3/H_2O_2 AOP will be highly efficient for the treatment of all chemicals in this study except RDX, which shows the lowest OH radical reactivity. Removal of a contaminant does not mean complete mineralization and reaction byproducts may be a problem if they are recalcitrant and are likely to cause health concerns.

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1. Introduction

The ozonation and ozone/hydrogen peroxide advanced oxidation process (O_3/H_2O_2 AOP) are recognized to be effective treatment processes to achieve degradation of contaminants in drinking water. The knowledge of chemical reaction kinetics is essential for predicting oxidation efficiencies of pollutants in these processes. During ozonation and O_3/H_2O_2 AOP, a pollutant (M) reacts both with O_3 (the direct reactions) and OH radicals (the indirect reactions) through second-order kinetics. Prediction of the extent of degradation through these two pathways relies on knowing the intrinsic second-order

rate constants for reactions of the pollutant with ozone ($k_{O_3,M}$) and OH radicals ($k_{OH,M}$). Although a large amount of kinetic data are available on the reaction rate constants of OH radicals and ozone with chemicals in aqueous solutions (Buxton et al., 1988), there is still a dearth of data especially for the emerging pollutants such as those on the US EPA's Drinking Water Contaminant Candidate List (CCL) (US EPA, 1998).

The objectives of the research were to determine the direct and indirect rate constants ($k_{O_3,M}$ and $k_{OH,M}$) and the treatability for nine chemicals on the CCL by ozonation and the O_3/H_2O_2 AOP. The pollutants studied include thiocarbamate,

triazine and urea herbicides, RDX and substituted benzene compounds. Results were compared with literature data and a parallel study using UV/H_2O_2 AOP (Shemer et al., 2006). The reactivity of the chemicals was correlated to their structures and reaction mechanisms.

2.   Methods

2.1.   Reagents

Most chemicals (>99% purity) were purchased from Chem Service Inc. (West Chester, PA, USA). RDX was from AccuStandard Inc. (CT, USA) sold as solution in acetonitrile (ACN). All chemicals were used as received without further purification. Stock solutions of the CCL chemicals were prepared in dichloromethane (DCM), except for RDX which was in ACN. Aqueous reaction solutions were prepared by dispensing an appropriate amount of the stock solution into a dry flask, and then blowing off the solvent by a gentle flow of nitrogen gas before the phosphate-buffered water was added. Reaction solutions were stirred overnight for complete chemical dissolution. All other stock solutions were prepared in Milli-Q nanopure water.

Aqueous ozone stock solutions were prepared by continuously bubbling ozone produced by an oxygen-feed (oxygen >99%) ozonator (OSMONICS OREC[TM] V Series, Phoenix, AZ, USA) into Milli-Q water chilled in an ice-water bath (Bader and Hoigné, 1981). The concentration of ozone stock solution was about $35\,mg\,L^{-1}$. pH of all experiments were adjusted by adding orthophosphate buffers (H_3PO_4/KH_2PO_4/Na_2HPO_4) so that the total phosphate concentration in the final solution was $0.02\,M$.

2.2.   Experiments

All experiments were performed in pH-buffered Milli-Q nanopure water at room temperature ($22\,°C$). Experimental setups and procedures are similar to those described in Chen et al. (2006).

The direct rate constants of diuron, linuron and RDX with ozone ($k_{O_3,M}$) were measured in a 1-L dispenser using solute consumption method under pseudo-first-order conditions. Initial concentrations of the CCL chemicals were about 0.5–$1\,\mu M$, and the applied ozone doses ranged from 1.8 to $4.4\,ppm$ (37.5–$91.7\,\mu M$). Hence, the ozone concentrations were in an approximate range of $37\times$ to $183\times$ excess. Furthermore, experiments were performed under acidic conditions (pH 2.4) and with $10\,mM$ tertiary butanol to minimize ozone decomposition and any OH radical reactions with the CCL chemicals. The reaction conditions were such that the ozone concentration remained relatively constant (usually $\leqslant 8\%$ decrease). The rate constants for the direct reaction were determined by monitoring chemical decay over time according to the following equation:

$$\ln\left(\frac{[M]_t}{[M]_o}\right) = -k_{O_3,M}[O_3]t. \tag{1}$$

The indirect rate constants of chemicals with OH radicals ($k_{OH,M}$) were determined by competition kinetics method.

Hydroxyl radicals were produced by using either ozonation at pH 8.2 (for ureas and RDX) or ozone combined with H_2O_2 at pH 7.2 (for the other CCL chemicals). In the ozonation experiments, an overall reaction rate constant (k) was first determined by monitoring chemical decay over ozone exposure ($\int[O_3]dt$) using Eq. (2). Ozone exposure can be calculated from the time kinetics of ozone during reaction. During the ozonation experiments, both direct and indirect reactions are taking place and the overall rate constants can be expressed by Eq. (3). R_{ct}, which is defined as the ratio between OH radical exposure and ozone exposure ($= \int[OH]dt/\int[O_3]dt$), is usually a constant value for a specific reaction system and can be viewed as the concentration ratio between OH radicals and O_3 (Elovitz and von Gunten, 1999). R_{ct} in an ozonation process was calculated by applying Eqs. (2) and (3) to a chemical with known $k_{OH,M}$ and $k_{O_3,M}$ values. With known R_{ct}, k and $k_{O_3,M}$ values (determined above), the $k_{OH,M}$ of CCL can be obtained through Eq. (3).

$$\ln\left(\frac{[M]_t}{[M]_o}\right) = -k\int_0^t [O_3]\,dt, \tag{2}$$

$$k = k_{OH,M}R_{ct} + k_{O_3,M}. \tag{3}$$

In the O_3/H_2O_2 experiments, the relative decay rate of a CCL chemical (M) to a reference compound (R) can be expressed as follows by applying Eqs. (2) and (3) to M and R:

$$\ln\left(\frac{[M]_t}{[M]_o}\right)\Big/\ln\left(\frac{[R]_t}{[R]_o}\right)$$
$$= (k_{OH,M}R_{ct} + k_{O_3,M})/(k_{OH,R}R_{ct} + k_{O_3,R}). \tag{4}$$

When k_{O_3} of the reference and the CCL chemical are very small, the above equation can be simplified as

$$k_{OH,M} = k_{OH,R} \times \ln\left(\frac{[M]_t}{[M]_o}\right)\Big/\ln\left(\frac{[R]_t}{[R]_o}\right). \tag{5}$$

Eq. (5) was applied for the calculation of $k_{OH,M}$. The initial concentrations of CCL chemicals were about $2\,\mu M$ and the applied H_2O_2 concentration was $0.1\,mM$. Six to eight ozone doses ranging from 0.5 to $5\,mg\,L^{-1}$ (ca. 0.01–$0.1\,mM$) were applied during the O_3/H_2O_2 experiments to create H_2O_2/O_3 molar ratios from 10 to 1.
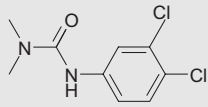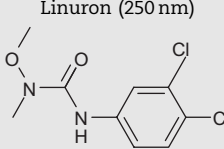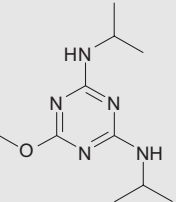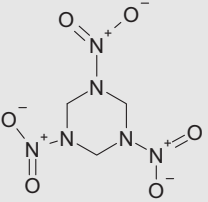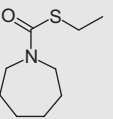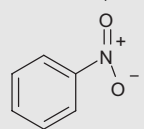
2.3.   Analytical methods

Dissolved ozone was measured using the indigo method (Bader and Hoigné, 1981). CCL chemical concentrations were monitored by routine HPLC-UV analyses. Samples ($50\,\mu l$ per injection) were directly injected into a Varian Pro Star HPLC (Varian, Inc., Palo Alto, CA, USA). A C18 column ($7.5 \times 150\,mm$) was used for separatio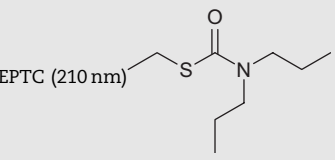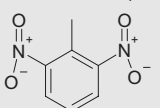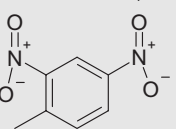n and ACN/water was used as the eluting solvent at a flow rate of $1\,mL\,min^{-1}$. Varian Model 330 UV detector was used for measuring the absorbance at different wavelengths shown in Table 1. The method detection limit is about $5\,nM$.

3.   Results and discussion

Results of $k_{O_3,M}$ and $k_{OH,M}$ for the CCL chemicals (see Table 1 for structures) are shown in Tables 2 and 3, respectively. Example calculations of $k_{O_3,M}$ and $k_{OH,M}$ are shown in

Table 1 – Chemical structures for the CCL chemicals studied

Groups	Chemical names and structures

Urea herbicides — Diuron (250 nm), Linuron (250 nm)

Triazine herbicide — Prometon (218 nm), RDX (250 nm)

Thiocarbamate herbicides — Molinate (210 nm), EPTC (210 nm)

Substituted benzenes — 2,6-Dinitrotoluene (210 nm), 2,4-Dinitrotoluene (242 nm), Nitrobenzene (259 nm)

Wavelength (λ_{max}) of the CCL chemical in HPLC measurement is indicated in the bracket next to each chemical's name.

Table 2 – Rate constants for direct reactions ($k_{O_3,M}$) of CCL chemicals with ozone

Compound names	pKa	pH	Temp. (°C)	$k_{O_3,M}$ (M^{-1} s^{-1}), this study	$k_{O_3,M}$ (M^{-1} s^{-1}), literature values
Diuron	N/A	2.4	22	13.3 ± 0.95[a]	14.7 ± 0.8[b]
Linuron		2.4	22	2.57	3.0[c]
RDX		2.4	22	0.97	
Prometon	4.3	3	25	~2[c]	
		7.5	20	< 12[c]	
EPTC	N/A	2	22	500[c]	
Molinate		2	22	500[c]	
Nitrobenzene					0.09 ± 0.02[d]
					2.2[e]
2,4-DNT		2	23	<14[c]	
2,6-DNT		2	23	<14[c]	5.7[e]

[a] Mean ± 1 × (standard error). Two experiments were performed where the standard errors were reported.
[b] From De Laat et al. (1996) (20 °C, pH 4, ozonation with competition kinetics of solutes).
[c] Estimated values (see the text for calculations and explanations).
[d] From Hoigné and Bader (1983) (23 °C, pH 2, ozonation with ozone consumption method).
[e] From Beltrán et al. (1998b) (20 °C, pH 2, ozonation with ozone consumption method).

Figs. 1–3. By comparing results from this study and those from the literature, we found that sometimes similar $k_{O_3,M}$ and $k_{OH,M}$ values were obtained even when different determination methods were used. While other times, similar determination method gave different results. For instance, similar $k_{O_3,M}$ values of linuron and diuron were obtained from this study by solute consumption method and from De Laat et al. (1996) by competition kinetics method. The solute consumption method can possibly overestimate the results due to some additional transformations of solutes by secondary radicals (but not OH radicals because they are quenched by tertiary butanol). However, the competition

Table 3 – Rate constants for indirect reactions ($k_{OH,M}$ ($M^{-1} s^{-1}$)) of the CCL chemicals with OH radicals

Groups	Chemical names	pH[a]	Ozonation and O_3/H_2O_2 (22 °C)		UV/H_2O_2 (22 °C)[b]		Literature values ($\times 10^9$)
			$k_{OH,M}$ ($\times 10^9$)	Ref. Comp.[c]	$k_{OH,M}$ ($\times 10^9$)	Ref. comp.[d]	
Ureas	Diuron	8.2	7.66 ± 0.39[e]	BB	7.5 ± 0.23	Molinate	4.6[f]
	Linuron	8.2	6.44 ± 0.30	BB	6.5 ± 0.28	Molinate	4.3[f]
RDX	RDX	8.2	0.25 ± 0.008	BB	(1.6 ± 0.19)[g]	NB	0.34[h]
Triazine	Prometon	7.2	2.6	2,4-DNT	2.5 ± 0.01	Molinate	
		7.2	2.53	Molinate			
Thiocarbamates	EPTC	7.2	(13.2 ± 0.5)[g]	NB			
	Molinate	7.2	(12.4 ± 0.2)[g]	NB and Prometon	6.9 ± 0.06	NB	1.3[i]
Substituted benzenes	Nitrobenzene						2.14[j] 3.9[i] 2.9[k]
	2,4-DNT	7.2	1.26 ± 0.02	NB			
	2,6-DNT	7.2	0.921	Prometon			0.75[k]
		7.2	0.996	Molinate			

[a] Experimental pH conditions.

[b] From Shemer et al. (2006).

[c] $k_{OH,M}$ values ($\times 10^9 M^{-1} s^{-1}$) of the reference compounds used are: bromobenzene (BB) = 5.3 (Chen et al., 2006), 2,4-DNT = 1.26 (this study), molinate = 12.4 (this study), prometon = 2.6 (this study) and nitrobenzene (NB) = 3.9 (Buxton et al., 1988).

[d] $k_{OH,M}$ values ($\times 10^9 M^{-1} s^{-1}$) used for the reference compounds are: molinate = 6.9 (Shemer et al., 2006) and nitrobenzene (NB) = 3.9 (Buxton et al., 1988).

[e] Mean $\pm 1 \times$ (standard error). Two experiments were performed where the standard errors were reported.

[f] From De Laat et al. (1996) (20 °C, ozonation at pH > 9.5 or O_3/H_2O_2 at pH > 8.2).

[g] Values were overestimated (see text for explanations).

[h] From Bose et al. (1998a) (estimated from a pilot study by UV/H_2O_2).

[i] From Buxton et al. (1988) (molinate by UV/H_2O_2; nitrobenzene by pulse radiolysis, 20 °C).

[j] From Armbrust (2000) (25 °C, UV/H_2O_2, pH 7).

[k] From Beltrán et al. (1998a) (20 °C, O_3/H_2O_2, pH 7).
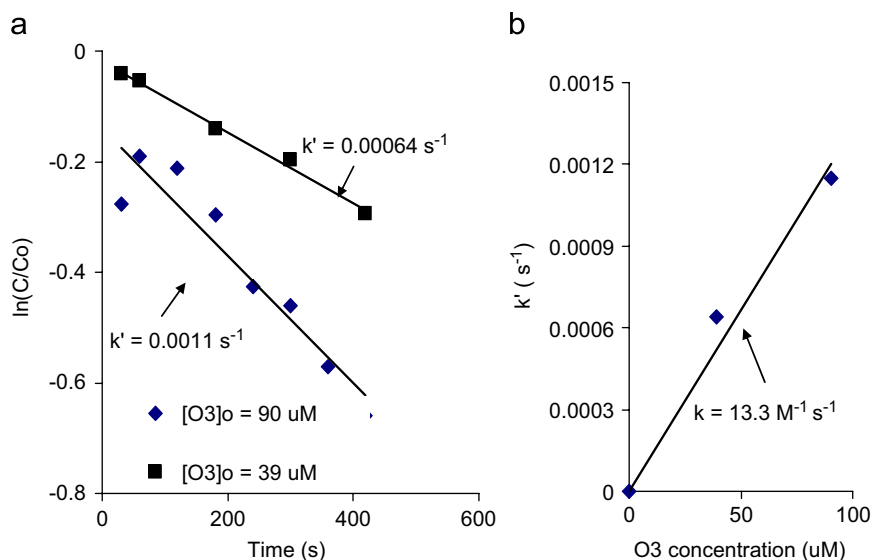
Fig. 1 – Determination of $k_{O_3,M}$ for diuron. (a) Change of $\ln(C/C_0)$ vs. time for diuron at different initial ozone concentrations. pH = 2.4; [diuron]$_0$ = 1.03 and 2.18 µM. A pseudo-first-order decay rate (k') is obtained. (b) Variation of k' with initial concentrations of ozone. $k' = k_{O_3,M}[O_3]_0$ (according to Eq. (1)). Second-order decay constant $k_{O_3,M}$ is the slope in (b).
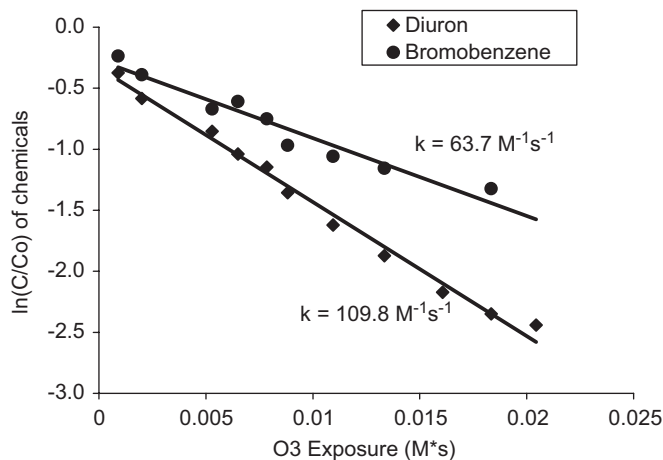
Fig. 2 – Determination of $k_{OH,M}$ by ozonation process at pH 8.2. [diuron]$_0$ = 0.86 μM, bromobenzene (BB) = the reference compound, [BB]$_0$ = 0.36 μM, [O$_3$]$_0$ = 33 μM. The overall second-order rate constants (k) of the CCL chemical and the reference are the slopes in the figure. R_{ct} in the ozonation process is calculated to be 1.2×10^{-8} by applying $k_{OH,BB}$ (5.3×10^9 M^{-1} s^{-1}) and $k_{O_3,BB}$ (0.16 M^{-1} s^{-1}) to Eq. (3). $k_{OH,M}$ of diuron is calculated by applying the known k and R_{ct} values to Eq. (3).
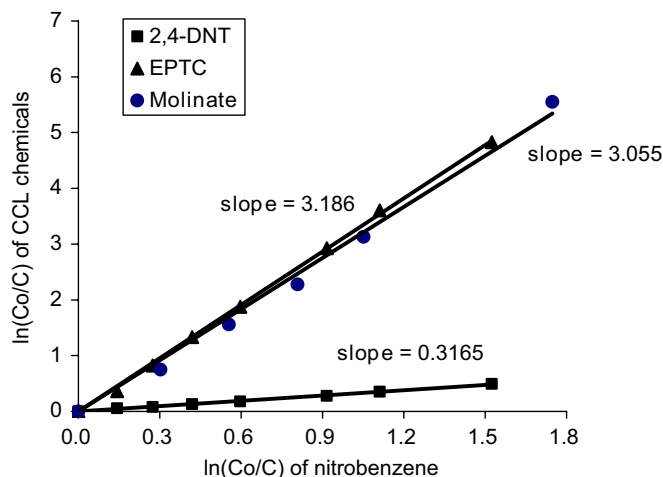
Fig. 3 – Determination of $k_{OH,M}$ for CCL chemicals using O$_3$/H$_2$O$_2$ AOP at pH 7.2. [EPTC]$_0$ = 2.3 μM, [2,4-DNT]$_0$ = 1.84 μM, [nitrobenzene]$_0$ = 2.0 μM, [H$_2$O$_2$]$_0$ = 0.1 mM, [O$_3$]$_0$ = 0, 0.5, 1, 1.5, 2, 3, 4 and 5 mg L^{-1} (or 0, 10, 21, 31, 42, 62, 83 and 104 μM). Decay rates of CCL chemicals are plotted against the decay rate of the reference compound. $k_{OH,M}$ is calculated by multiplying $k_{OH,M}$ of the reference (nitrobenzene) and the slope obtained (see Eq. (5)).

kinetics method is sensitive to the $k_{O_3,M}$ values of the reference compounds used. Similar results by different methods usually suggest similar reaction mechanisms (sometimes it is an overall expression of several reaction channels in competition), and that the interferences (or drawbacks) in each method are negligible.

The $k_{OH,M}$ values of the ureas from this study are higher than those from De Laat et al. (1996), though the same method and similar reaction conditions were used. The differences may reflect differences in the experimental setups, sample handling, analytical methods used and machine performance. Sometimes it may also reflect differences in the balance among the different reaction channels in operation. The reaction rates measured following the disappearance of the starting material indicate how fast the starting material reacts but gives no indication about the possibility of the occurrence of several reaction channels in

competition. Hence, the measured rate constants of a given compound with ozone or hydroxyl radicals are a combination of the rate constants of the individual reaction channels occurring in competition.

The $k_{OH,M}$ value of 2,6-DNT measured by competition kinetics method during O$_3$/H$_2$O$_2$ is higher than that from Beltrán et al. (1998a) using absolute kinetics method by mass transfer principles. This is because our study used a higher $k_{OH,NB}$ value (see Table 3) as the reference. However, the k_{OH} ratios of NB and 2,6-DNT in both studies are similar (3.9 vs. 4.1), indicating results are comparable between the two studies.

The $k_{OH,M}$ results from this study and from a parallel study using UV/H$_2$O$_2$ process (Shemer et al., 2006) should be more comparable since samples were handled in the same way and were analyzed on the same machine. However, many chemicals in this study (including molinate, the reference

compound) undergo significant direct photolysis reactions (over the OH radical reaction) during the UV/H$_2$O$_2$ process. Although a new method was established by Shemer et al. (2006) to account for the effect of direct photolysis, there is still uncertainty in the $k_{OH,M}$ values obtained in this way. In contrast, the ozonation and O$_3$/H$_2$O$_2$ AOP used in this study are mostly OH radical-dominant processes. Except for the thiocarbamates, the $k_{O_3,M}$ values of the CCL chemicals studied (see Table 2) are so low that the interference of the direct reactions is negligible during the determination of $k_{OH,M}$. The matching $k_{OH,M}$ values of ureas by UV/H$_2$O$_2$ and by ozonation, especially that of linuron whose direct photolysis pathway is significant ($k'_d = 1.25 \times 10^{-3}$ cm^2 mJ^{-1}, Shemer et al., 2006), demonstrate that the new method by Shemer et al. (2006) is efficient in accounting for the effect of direct photolysis. However, for RDX ($k'_d = 4.7 \times 10^{-3}$ cm^2 mJ^{-1}, Shemer et al., 2006), in which the direct photolysis is dominant over the OH radical pathway, the new method seems to be not sufficient. On the other hand, the $k_{OH,M}$ value of molinate by O$_3$/H$_2$O$_2$ is not consistent with that by UV/H$_2$O$_2$, which is probably due to interference from its significant direct O$_3$ reactions. Prometon has very slow direct photolysis and direct O$_3$ reactions, and the two methods (UV/H$_2$O$_2$ and O$_3$/H$_2$O$_2$) agree well.

The use of O$_3$/H$_2$O$_2$ AOP in the determination of $k_{OH,M}$ values of molinate and other chemicals with fast direct O$_3$ reactions is therefore not recommended. Even if very high pH and H$_2$O$_2$ concentrations are applied, it is still uncertain if there are interferences from the direct O$_3$ reactions. Literature has given three different $k_{OH,M}$ values of molinate (see Table 3) by using UV/H$_2$O$_2$ method. Therefore, $k_{OH,M}$ value of molinate needs to be confirmed preferably by another method (e.g. pulse radiolysis).

The $k_{O_3,M}$ values of prometon, 2,4-DNT and 2,6-DNT were estimated by correlating them with compounds of similar structures and by the electrophilic natural of the direct O$_3$ reactions. Similar rates can be derived if reactions take place at the same functional groups. Electron-releasing or withdrawing property of the adjacent groups can also significantly alter the reaction rates by making the reaction sites more or less electrophilic for O$_3$ attacks. The $k_{O_3,M}$ values of molinate and EPTC were calculated by applying the R_{ct} concept (Elovitz and von Gunten, 1999). These estimates can provide the orders of magnitude of the reaction rates, which can be of value in many ways.

3.1. Urea herbicides

Both diuron and linuron show low reactivity toward ozone indicated by small $k_{O_3,M}$ values. The small rate constants indicate that ozonation at low pH will not be effective in degrading these compounds. Assuming that the reactivity of both compounds is due to O$_3$ attack at the aromatic ring, the low reactivity can be explained as due to the two electron-withdrawing Cl groups on the benzene ring, which decrease the electron density of the ring and hence decrease the electrophilic attack by ozone. This is also supported by lower reaction rates of diuron and linuron (dichlorinated ureas) compared to their corresponding monochlorinated analoges (monouron and monolinuron) under more molecular (i.e. direct O$_3$ reaction) conditions (O$_3$/H$_2$O$_2$, pH 5.6) (Tahmasseb

et al., 2002). Under more radical (i.e. indirect reaction) conditions (O$_3$/H$_2$O$_2$, pH 7), the dichlorinated ureas react faster than their monochlorinated analoges (Tahmasseb et al., 2002). Diuron shows a much higher O$_3$ reactivity (a five-fold difference) than linuron. It was also found by Tahmasseb et al. (2002) that N-dimethylureas were more reactive than their N-methyl, N-methoxy counterparts at low pH.
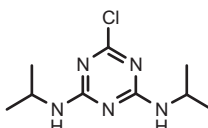
Unlike the rate of direct ozone reactions, the indirect radical reaction rate of diuron is only slightly higher than that of linuron. Product study (Tahmasseb et al., 2002) shows that the primary OH radical reaction for diuron is through N-demethylation (to form mono N-demethylated diuron) rather than by OH addition to the aromatic ring. With linuron, N-demethylation accompanied by elimination of N-methoxy group (to form 3,4-dichlorophenylurea) is a more important pathway. Both linuron and diuron have high OH radical reactivity (on the order of 10^9), therefore they can be efficiently removed by processes that mainly involve OH radical reactions (e.g. O$_3$/H$_2$O$_2$, UV/H$_2$O$_2$ and ozonation at high pH). Meijers et al. (1995) reported 98% and 89% removal for diuron and linuron, respectively, at pH 8.3 with O$_3$/DOC ratio of 1.0 using ozone bubbling column.

3.2. RDX

RDX shows low reactivity toward ozone and OH radicals as demonstrated by its low $k_{O_3,M}$ and $k_{OH,M}$ values. Its ring structure and the highly oxidized nitro groups are resistant to ozone and OH radical oxidation. Given the very low reactivity with ozone and OH radicals, RDX is not expected to be efficiently removed in an ozonation or O$_3$/H$_2$O$_2$ operation. Bose et al. (1998a) reported that the O$_3$/H$_2$O$_2$ process, using a H$_2$O$_2$/O$_3$ ratio of 0.35 g/g, was effective at oxidizing RDX with a $t_{1/2}$ of 1.2 min (vs. $t_{1/2}$ of 115 min for ozone alone at pH 7.2). However, that experiment employed high ozone and H$_2$O$_2$ doses (e.g. 16 mg L^{-1} O$_3$ and 5.6 mg L^{-1} H$_2$O$_2$ to achieve 99% RDX removal). Under less aggressive AOP operation (e.g. OH radical CT for 90% removal of MIB), only a 7% removal of RDX could be expected. Worth noting, however, is the potential use of direct photolysis for RDX treatment because of its fast direct photolysis rate ($k'_d = 4.7 \times 10^{-3}$ cm^2 mJ^{-1}, Shemer et al., 2006). Product study shows that hydroxyl radicals would probably attack the amine nitrogen of RDX; hydroxyl radicals would also promote the cleavage of the heterocyclic ring during AOPs (Bose et al., 1998b).

3.3. Triazine herbicide

Prometon is also expected to have low reactivity toward ozone. The triazine ring is very resistant to oxidation, and hence reactivity of prometon toward ozone will likely be dictated by side chains. Barletta et al. (2003) found that N-dealkylated triazine is the major reaction product of propazine with ozone molecules, probably by electrophilic attack of ozone at one of the amine

nitrogens. Prometon is very likely to react with ozone in a similar fashion. Therefore, the O_3 reaction rate of prometon is expected to be close to that of propazine: $k_{O_3,M} = 1.53\,M^{-1}\,s^{-1}$ at pH 3 and 25 °C (Barletta et al., 2003). The $k_{O_3,M}$ of propazine was measured under conditions in which both the unprotonated and the protonated forms of triazine were present (Almost no reactions were observed at pH 0 where only the protonated form existed in solution.) (Barletta et al., 2003). Therefore, the O_3 reactivity of prometon under neutral and basic solutions, where only the unprotonated form exist is expected to be higher. Xiong and Graham (1992) has reported $k_{O_3,M}$ of $12.2\,M^{-1}\,s^{-1}$ (at 20 °C) at pH 7.5 for atrazine
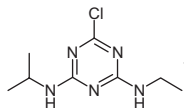
. The $k_{O_3,M}$ of unprotonated prometon will be lower than that of atrazine at similar conditions because: (1) ozone reacts faster with atrazine than with propazine (Barletta et al., 2003); and (2) $k_{O_3,M}$ of atrazine was likely overestimated due to radical reactions occurring at pH 7.5 (Xiong and Graham, 1992).

Despite of the low ozone reactivity, prometon shows reasonable reactivity toward OH radicals and thus can be efficiently degraded by the OH radical dominated treatment processes. Byproducts of the TiO_2-mediated photooxidation of prometon show that prometon was oxidized by OH radicals primarily through N-deisopropylation and may be also through the substitution of the methoxy group by a hydroxyl group (Borio et al., 1998). These pathways are very much comparable to that of atrazine during O_3/H_2O AOP (Nélieu et al., 2000); the $k_{OH,M}$ value of prometon ($2.6 \times 10^9\,M^{-1}\,s^{-1}$) is also similar to that of atrazine ($3 \times 10^9\,M^{-1}\,s^{-1}$) (Acero et al., 2000).

3.4. Thiocarbamate herbicides

The $k_{OH,M}$ values of molinate and EPTC measured by O_3/H_2O_2 are considerably higher than those measured by UV/H_2O_2 in the literature (see Table 3). The greater value is likely due to the negligence of the fast direct ozone reactions of the molinate in the calculation of $k_{OH,M}$ using conventional competition kinetics method where $k_{O_3,M}$ of both the reference and the substrate compound are ignored (see Eq. (5)). This likely occurred in the measurement of $k_{OH,M}$ value for EPTC as well. The nucleophilic S atom of both thiocarbamates is highly reactive toward O_3, and the $k_{O_3,M}$ for simple alkyl sulfides (–RSR'(or H)–) are usually around or greater than 10^4–$10^5\,M^{-1}\,s^{-1}$ (Yao and Haag, 1991; Hoigné and Bader, 1983). However, the $k_{O_3,M}$ of molinate and EPTC are expected to be lower because the lone pair of S electrons can be conjugated with the adjacent C=O double bond and thus makes it less available for reaction. Furthermore, the C=O group, which is electron withdrawing, can also decrease the electron density of S to make it less electrophilic (i.e. less O_3 reactive).

It is interesting to observe that although the $k_{OH,M}$ of molinate measured by O_3/H_2O_2 ($1.2 \times 10^{10}\,M^{-1}\,s^{-1}$) is potentially as much as $10\times$ too large, the use of this value in Eq. (5) for molinate as a reference compound still gave consistent results for measuring $k_{OH,M}$ of prometon and 2,6-DNT in O_3/H_2O_2 experiments with other reference compounds (see Table 3). This is because nitrobenzene, which has low O_3 reactivity ($k_{O_3,M}$ can be ignored in calculations), was used as a reference compound for measuring $k_{OH,Molinate}$. Therefore, $k_{OH,M}$ of prometon and 2,6-DNT (both with low O_3 reactivity) can be calculated as if nitrobenzene was used as their reference compound by further multiplying the slope of molinate in Fig. 3. However, we will not obtain correct $k_{OH,M}$ values for an O_3 reactive chemical if molinate is used as the reference compound in the O_3/H_2O_2 experiments using competition kinetics method. Furthermore, if an alternative $k_{OH,Molinate}$ value (e.g. one from the literature) was used in the calculation, we would obtain wrong $k_{OH,M}$ values for prometon and 2,6-DNT. Therefore, special caution needs to be given to compounds with high ozone reactivity (either as reference or as substrate) when $k_{OH,M}$ is determined using Eq. (5).

If $k_{O_3,Molinate}$ is not neglected in the calculation of $k_{OH,Molinate}$ (with nitrobenzene (NB) as the reference compound), the relationship between the true $k'_{OH,Molinate}$ value and the overestimated value (we name it $k_{OH,Molinate}$) is

$$k'_{OH,Molinate} = \text{Slope of Molinate in Figure (3)} \times k_{OH,NB}$$
$$= k_{OH,Molinate} + k_{O_3,Molinate}/R_{ct}. \tag{6}$$

A constant slope of molinate ($R^2 > 0.99$) indicates that the R_{ct} remains constant as the O_3 doses increased from 0.5 to $3\,mg\,L^{-1}$ (H_2O_2/O_3 molar ratios from 10 to 1.6) in the O_3/H_2O_2 process. Assuming $R_{ct} = 10^{-7}$ (Chen et al., 2006) and $k_{OH,Molinate} = 6.9 \times 10^9\,M^{-1}\,s^{-1}$ (Shemer et al., 2006), the estimated $k_{O_3,Molinate}$ equals $500\,M^{-1}\,s^{-1}$ by using Eq. (6). The ozone reactivity of EPTC is expected to be comparable to that of molinate because of their similar chemical structures. Both chemicals can be fast degraded by conventional ozonation and by the OH radical-dominated treatment processes.

3.5. Nitrotoluenes and nitrobenzene

The basic direct ozone reaction with aromatic compounds is by electrophilic aromatic substitution reaction because of the stability of the aromatic ring (Beltrán, 2004). Low $k_{O_3,M}$ values of these chemicals are expected since the strong electron-withdrawing nitro substitutions decrease the electron-density of the aromatic rings and thus lower their O_3 reactivity. Beltrán et al. (1998a) found that $k_{O_3,M}$ value of 2,6-DNT is higher than that of NB due to the electron releasing methyl group that activates the ring during ozone reactions. The $k_{O_3,M}$ value of NB as measured by Beltrán et al. (1998b) ($2.2\,M^{-1}\,s^{-1}$) is more than 20 times higher than that by Hoigné and Bader (1983) ($0.09\,M^{-1}\,s^{-1}$). We have previously measured the $k_{O_3,M}$ of bromobenzene to be $0.16\,M^{-1}\,s^{-1}$ (Chen et al., 2006). Since a nitro group is much more electron-withdrawing than a bromo group, lower $k_{O_3,M}$ value is expected for nitrobenzene than for bromobenzene. It seems that the $k_{O3,NB}$ measured by Beltrán et al. (1998b) was overestimated. Because of the strong electron-withdrawing effect of the nitro substituents, $k_{O_3,M}$ of both 2,4-DNT and 2,6-DNT should be lower than that of toluene (which has no nitro groups, $k_{O_3,toluene} = 14 \pm 3\,M^{-1}\,s^{-1}$ at 23 °C (Hoigné and Bader, 1983)).

Despite of their low ozone reactivities, all three substituted benzenes are quite reactive toward OH radicals and thus can be efficiently treated during the OH radical predominated processes. $k_{OH,M}$ of 2,4-DNT is slightly higher than that of its

isomer 2,6-DNT. The same order is observed in the UV/Fenton system and is attributed to the steric constraints imposed on the methyl group by the 2,6-DNT configuration rather than the 2,4-DNT configuration (Li et al., 1998). The OH radical attack of the DNTs is usually considered to occur by methyl group oxidation and followed by hydroxylation (Li et al., 1998). This is supported by Beltrán et al. (1998a, b) who found 2,6-dinitrobenzaldehyde to be a common product from OH radical oxidation of 2,6-DNT. However, the OH radicals react with NB by addition to the ring to form nitrophenols (and other products) (Beltrán et al., 1998a, b); OH radical reaction of NB is faster than that of the DNTs.

4. Conclusions

Nine chemicals on the US EPA's Contaminant Candidate List were studied for their reactivity with ozone and OH radicals during the ozonation and O_3/H_2O_2 AOP process. Second-order reaction rate constants with ozone and OH radicals ($k_{O_3,M}$ and $k_{OH,M}$) were either measured or estimated from structure/activity relationships with regard to the reaction mechanisms. The urea herbicides (linuron and diuron), triazine (prometon), RDX and substituted benzene compounds (nitrobenzene, 2,4-dinitrotoluene and 2,6-dinitrotoluene) show low reactivity toward ozone, whereas the thiocarbamates (molinate and EPTC) are highly reactive toward O_3 due to the O_3 reactive S atom. All chemicals (except RDX) demonstrate high reactivity toward OH radicals.

In the water treatment application, only the thiocarbamate herbicides can be efficiently treated by ozonation at low pH, which involves mainly the direct ozone reactions. Ozonation at high pH and O_3/H_2O_2 AOP will be highly efficient for the removal of the thiocarbamates, ureas, prometon and substituted benzenes. However, product studies show that most chemicals are unlikely to be mineralized and the reaction byproducts may be a problem if they are likely to cause health concerns. RDX is more resistant to ozonation and O_3/H_2O_2 AOP than any other CCLs in this study.

Acknowledgments

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