

Hydroxyl radical rate constants: comparing UV/H₂O₂ and pulse radiolysis for environmental pollutants

Michael S. Elovitz, Hilla Shemer, Julie R. Peller, K. Vinodgopal, Mano Sivaganesan and Karl G. Linden

ABSTRACT

The objective of this study was to measure hydroxyl radical reaction rates using both UV/H₂O₂ and pulse radiolysis techniques for 10 US EPA Contaminant Candidate List compounds (2,6- and 2,4-DNT, EPTC, prometon, linuron, diuron, RDX, molinate, nitrobenzene, and terbacil). The rate constants determined using these techniques were compared to each other and to values reported in the literature. Difference factors between k_{OH} obtained using UV/H₂O₂ and pulse radiolysis ranged from 1.1 to 4.7. It was shown that even small differences in hydroxyl radical rate constants values can result in fairly large differences (up to 50%) when trying to predict removals of pollutants in an advanced oxidation process.

Key words | competition kinetics, contaminant candidate list, oxidation, photolysis, ultraviolet (UV) irradiation

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INTRODUCTION

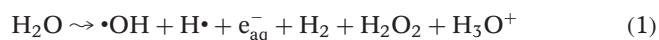
The US EPA Contaminant Candidate List (CCL) specifies unregulated priority contaminants and pathogens for the Agency's drinking water program. The CCL comprises several different classes of chemical compounds, and it is widely recognized that no single treatment technology can be applicable to all of them. For example, granular activated carbon adsorption may be very effective for removing hydrophobic compounds, but this method works poorly for very volatile or water soluble compounds. Furthermore, traditional methods all have known drawbacks. Activated carbon adsorption and air stripping are common water treatment technologies that merely transfer the organic pollutant from one phase to another. Biological treatment of wastewater is able to degrade many organic pollutants but is usually only economical for relatively high strength wastewaters and biodegradable compounds (Nacheva *et al.*

2000; Zhou *et al.* 2006). In contrast, advanced oxidation processes (AOPs) are generally applicable for destroying a broad spectrum of chemicals.

Over the past 25 years there has been a growing awareness that the treatment of many pollutants by AOPs can be both efficient and economical. AOPs represent those technologies which bring about enhanced oxidative degradation of pollutants in aqueous solution by the generation of highly reactive intermediates (e.g., the hydroxyl radical) via several methods. In some, an external energy source is used such as ultraviolet (UV) irradiation or radiolysis, and in others the process is driven by chemical energy (e.g., O₃/H₂O₂, Fe²⁺/H₂O₂). AOPs can complement or even replace conventional treatment processes since they are able to treat and destroy organic (Beltran *et al.* 1998; Bose *et al.* 1998; Acero *et al.* 2000; Shemer & Linden 2007) and

some inorganic pollutants (e.g., cyanide (Monteagudo *et al.* 2004; Sarla *et al.* 2004)) even at low concentrations (Goel *et al.* 2004). For these reasons, AOPs may prove useful for treating contaminated drinking water.

Pulse radiolysis is regarded as a very accurate method for measuring absolute (bimolecular) rate constants for reaction between hydroxyl radicals ($\bullet\text{OH}$) and organic contaminants (k_{OH}). In this method highly reactive species e_{aq}^- , $\bullet\text{H}$, and $\bullet\text{OH}$, as well as inert or less reactive products H_2 , H_3O^+ , and H_2O_2 are formed as a result of decomposition of the water due to deposit of energy into the aqueous solution, according to the following equation:



On the short timescales at which radical chemistry occurs, only the three radical species, the oxidizing $\bullet\text{OH}$, the reducing hydrated electron (e_{aq}^-), and the hydrogen atom ($\bullet\text{H}$) react with chemicals in the water (Allen 1961). Pulse radiolysis experiments can involve direct measurements by monitoring the formation of the transient reaction product, or by competition kinetics wherein the formation of the transient of a reference compound is monitored instead of the transient of the substrate. In either case, a measurable concentration of hydroxyl radical is produced in a very reproducible manner by a pulse of high energy.

Hydroxyl radicals can also be produced by methods employing less sophisticated instruments. In a UV/ H_2O_2 process, hydroxyl radicals are generated by photolysis of the peroxide bond of H_2O_2 according to Equation (2).



Hydrogen peroxide is a fairly weak absorber of UV light [$\epsilon_{\text{max}}(200 \text{ nm}) = 198 \text{ M}^{-1} \text{ cm}^{-1}$], but its photolysis occurs with a quantum yield of 1.0 (Baxendale & Wilson 1957) resulting in steady state levels of $\bullet\text{OH}$ radicals of 10^{-15} to 10^{-12} M , depending on the hydrogen peroxide dose, water matrix and UV source emission spectra and strength. While the steady-state concentration of $\bullet\text{OH}$ radicals can be estimated based on UV photon flow (see calculation below), it is far easier to measure the rates of reaction between $\bullet\text{OH}$ radicals and the substrate by competition kinetics. As when competition kinetics is used with pulse

radiolysis, both the organic solute and a reference compound are present in the reaction mixture, and the organic solute competes with the reference compound for $\bullet\text{OH}$.

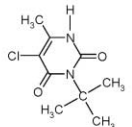
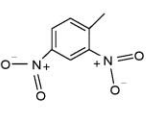
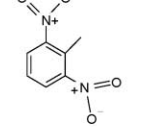
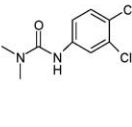
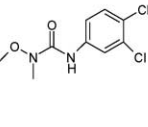
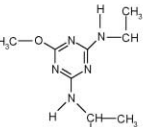
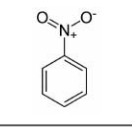
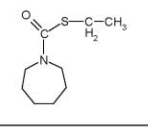
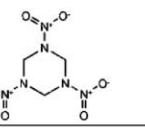
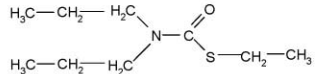
The goal of this study was to measure $\bullet\text{OH}$ radical rates using both UV/ H_2O_2 and pulse radiolysis techniques for 10 US EPA Contaminant Candidate List compounds: 2,6-dinitrotoluene (2,6-DNT) and 2,4-dinitrotoluene ($\text{C}_7\text{H}_6\text{N}_2\text{O}_4$), EPTC (S-ethyl dipropyl(thiocarbamate); $\text{C}_9\text{H}_{19}\text{NOS}$), prometon ($\text{C}_{10}\text{H}_{19}\text{N}_5\text{O}$), linuron ($\text{C}_9\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2$), diuron ($\text{C}_9\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}$), RDX (cyclotrimethylene-trinitramine; $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$), molinate ($\text{C}_9\text{H}_{17}\text{NOS}$), nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$), and terbacil ($\text{C}_9\text{H}_{13}\text{ClN}_2\text{O}_2$). The molecular structures of the compounds studied are shown in Table 1. The rate constants determined using these techniques were compared to each other and to values reported in the literature and indicated potentially important issues regarding AOP design and control.

METHODS

Materials

Reagent grade compounds were purchased from Chem Service Inc. (PA, USA); Sigma-Aldrich, (WI, USA);

Table 1 | Molecular structure of the CCL compounds studied

Terbacil 	2,4-dinitrotoluene 	2,6-dinitrotoluene 
Diuron 	Linuron 	Prometon 
Nitrobenzene 	Molinate 	RDX 
EPTC 		

AccuStandard Inc. (CT, USA); and Fluka, (Buchs, Switzerland). All chemical were at least 99% purity and were used as received.

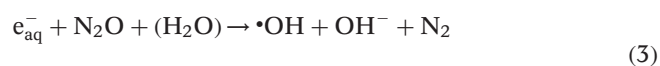
Experimental setup

UV/H₂O₂ Experiments with the UV/H₂O₂ process were conducted at room temperature in 20 mM phosphate buffered Milli-Q water (pH 7). Photolysis was carried out with a medium pressure mercury (MP) lamp (Hanovia Co., Union, NJ) emitting polychromatic UV irradiation in the 200 to 400 nm range and housed in a bench-scale collimated beam apparatus. A 100 mL sample was irradiated with gentle stirring in a crystallization dish (70 × 50 mm, 34.2 cm² surface area, solution depth approximately 3.3 cm) open to the atmosphere. The solutions were exposed to UV fluences of up to 300 mJ cm⁻² (200–300 nm basis) in the presence of hydrogen peroxide concentrations ranging from 0 to 50 mg L⁻¹. The initial concentration of the compounds studied as well as the reference compound was 2 μM in all experiments. The exposure times necessary to achieve the desired fluence were determined from the average irradiance, which was calculated with a spreadsheet program that considers the lamp spectrum, solution absorbance, incident irradiance reading from a calibrated radiometer (1700 IL, International Light), and the measured Petri-factor for the dish, 0.96, as per Bolton & Linden (2003).

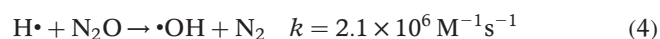
Pulse radiolysis

Pulse radiolysis experiments were conducted at the linear accelerator (LINAC) electron pulse radiolysis system at the Department of Energy Radiation Laboratory, University of Notre Dame. These irradiation and transient absorption detection systems have been described in detail previously (Whitham *et al.* 1995). To measure only the reactions of the •OH, all solutions were pre-saturated with nitrous oxide (N₂O) to remove dissolved oxygen gas and to quantitatively convert the hydrated electrons and hydrogen atoms to •OH according to Equations 3 and 4. The fast scavenging of e_{aq}⁻ ensures conversion to •OH within a few nanoseconds. Due to the relatively slow scavenging of H• by N₂O, total yield of H• is approximately 10% of the •OH yield. As such, an adduct formed from reaction between the substrate and

H• could potentially add to the total measured absorbance (i.e. the trace). Although H• generally reacts markedly slower with organic compounds than •OH, the potential for interference will depend on the ratio of those two reaction rates as well as the ratio of the extinction coefficients of the H• and •OH adducts at the monitored wavelength. Generally speaking, the total contribution of an H• adduct to the signal is typically less than 2% (Ashton *et al.* 1995). As with many pulse and gamma radiolysis studies, the rate constants measured in this study have not been corrected for any potential H• reaction pathways.



$$k = 9.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$



During rate constant measurements the solution vessel was sparged with only the minimum amount of N₂O necessary to prevent air ingress. Solution flow rates in these experiments were adjusted to ensure that each irradiation was performed on a fresh sample. Dosimetry (Buxton & Stuart 1995) was performed using N₂O-saturated, 1.00 × 10⁻² M KSCN solutions at λ = 475 nm, (G_e = 5.2 × 10⁻⁴ m²J⁻¹) with average doses of 3–5 Gy per 2–3 ns pulse. A value of k_{OH/SCN-} = 1.060 × 10¹⁰ M⁻¹s⁻¹ (at 18°C), was used for the rate constant of SCN⁻ and •OH radical forming the reaction product (SCN₂)⁻. All kinetics experiments were performed at ambient temperature (18 ± 1°C) and in MilliQ water. Each kinetic trace was the average of at least 15 pulses. Direct measurement of the transients was typically performed at the maximum absorbance of the transient. For eight of the compounds, the initial concentration of the substrate was at least >40 μM, and thus pseudo-first-order conditions ([substrate]₀ ≥ 10 × [•OH]₀) were achieved. Competition kinetics, using KSCN as the reference compound, was used for two compounds (RDX and molinate). The initial concentration of KSCN was 0.1245 mM and the initial concentration of the substrate was 0.225 mM (RDX) and 0.526 mM (molinate). The reaction was monitored by following the formation of (SCN₂)⁻.

Analytical methods

Aqueous samples from experiments conducted using UV/H₂O₂ were analyzed using HPLC equipped with a photodiode array detector and a reverse phase C-18 column (7.5 × 150 mm) run isocratically on a Varian Prostar HPLC (Varian, Inc., Palo Alto, CA). The eluent conditions varied depending on the compound, but consisted of acetonitrile and HPLC grade water in all cases. Calibrations were made using aqueous dilutions of analytical standards dissolved in methanol. Concentrations of the substrate in the pulse radiolysis experiments were confirmed by direct measurement of the UV-vis absorbance of the solution.

RESULTS AND DISCUSSION

*k*_{OH} calculation

Using the UV/H₂O₂ process, a competition kinetics experiment was conducted to evaluate the second-order rate constants for the reaction of hydroxyl radical with the pollutants. In this method, the relative rates of reaction of the pollutant and a reference compound are measured in a mixture. The pollutant and reference compound compete for hydroxyl radicals, and based on the known reactivity of the reference compound toward the hydroxyl radical, the rate constant for reaction of the pollutant can be determined (Einschlag *et al.* 2003). The simplest analysis uses Equation (5), which assumes reaction with hydroxyl radical is the only significant decay pathway.

$$k_{\text{OH(s)}} = \frac{k_s}{k_{\text{ref}}} \times k_{\text{OH(ref)}} = \frac{\ln([s]/[s]_0)}{\ln([\text{ref}]/[\text{ref}]_0)} \times k_{\text{OH(ref)}} \quad (5)$$

Here, *k_s* is the time-based observed pseudo-first-order rate constant for reaction of the pollutant and *k_{ref}* is the observed pseudo-first-order rate constant for reaction of the reference compound. A plot of ln([s]/[s]₀) versus ln([\text{ref}]/[\text{ref}]₀) gives a straight line passing through the origin with a slope equal to the ratio of the rate constants, *k_s*/*k_{ref}*. Figure 1 presents data for prometon obtained during competition kinetics experiments using UV/H₂O₂ with molinate as a reference compound. In UV/H₂O₂ systems, where both hydroxyl radical reactions and direct photolysis

contribute to the compound decay, pollutant degradation kinetics can be described by Equation (6).

$$-\frac{d[s]}{dt} = k'_{\text{d(s)}}[s] + k_{\text{OH(s)}}[\bullet\text{OH}]_{\text{ss}}[s] \quad (6)$$

where, *k'*_{d(s)} is the time-based pseudo-first-order direct photolysis rate constant and [OH]_{ss} is the steady-state concentration of hydroxyl radicals.

If direct photolysis plays a significant role in pollutant degradation during the UV/H₂O₂ process, it is necessary to subtract the rate of direct photolysis from the observed rate to determine the rate of the hydroxyl radical degradation. In this case, the analysis of competition kinetics data can be done using Equation (7).

$$k_{\text{OH(s)}} = \frac{\left(k_s - \left[\frac{E'_{\text{avg(H}_2\text{O}_2)}}{E_{\text{avg(w/o H}_2\text{O}_2)}} \right] k'_{\text{d(s)}} \right)}{\left(k_{\text{ref}} - \left[\frac{E'_{\text{avg(H}_2\text{O}_2)}}{E_{\text{avg(w/o H}_2\text{O}_2)}} \right] k'_{\text{d(ref)}} \right)} k_{\text{OH(ref)}} \quad (7)$$

where, *E'*_{avg(H₂O₂)/*E*_{avg(w/o H₂O₂)} is the ratio of the average irradiance with hydrogen peroxide to that without hydrogen peroxide. This term is essentially a weighting factor that corrects for the fact that the addition of hydrogen peroxide decreases the average irradiance received by the target contaminant through light screening effects, and thus reduces the rate of direct photolysis relative to that which occurs in the absence of hydrogen peroxide. In a collimated beam apparatus the average irradiance is the same as the average fluence rate (mW cm⁻²). Details regarding}

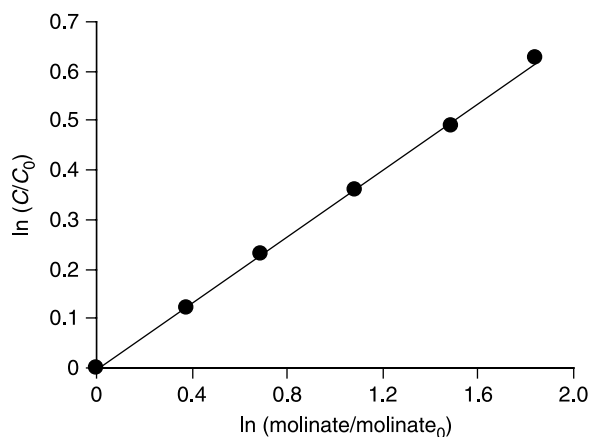


Figure 1 | Competition kinetics plot for prometon with molinate as a reference compound using UV/H₂O₂. Conditions were pH 7.2, [H₂O₂] 50 mgL⁻¹, prometon, molinate 2.0 μM.

Equation (7) are given elsewhere (Shemer *et al.* 2006). Note that this form of the equation differs from that reported in Shemer *et al.* (2006) in that Equation (7) uses the time-based pseudo-first-order rate constants (as opposed to the fluence-based rate constants shown in the citation). The use of Equation (5) or Equation (7) depends on whether the reference compound or pollutant undergoes significant direct photolysis. Of the CCL compounds studied, EPTC, RDX and linuron showed significant reactivity via direct photolysis. Molinate, used as a reference compound for several compounds in this study, also displayed enough direct photolysis under these experimental conditions that Equation (7) was sometimes warranted. In contrast, nitrobenzene, the other probe compound used, showed insignificant direct photolysis in these experiments. For consistency, k_{OH} values for all compounds were calculated using Equation (7).

Duplicate UV/H₂O₂ kinetic experiments were performed for each experimental condition. A final value of the pseudo-first-order rate constant for each experimental condition was calculated as the mean ($n = 2$ values) \pm the standard deviation. Further error calculations based on Equation (7), for the UV-based reactions, employed standard propagation of errors techniques (Taylor 1982) using the standard deviation of the mean of the pseudo-first-order rate constants and treating all other variables (i.e. $k_{\text{OH(ref)}}$, $E_{\text{avg(H}_2\text{O}_2)}^i$ and $E_{\text{avg(w/o H}_2\text{O}_2)}^i$) as constants (i.e. zero uncertainty).

In the pulse radiolysis experiments, triplicate kinetic traces were recorded at each of 4 or 5 different initial concentrations of the substrate. Each kinetic trace was the average of at least 15 pulses. For experiments where the rate constant was measured directly, the overall second-order rate constant and its associated uncertainty estimate was determined by simultaneously modeling all individual traces to the first-order formation rate expression

$$A = C(1 - \exp(-k_{\text{obs}}t)) + \varepsilon \quad (8)$$

and total of all traces to the second-order rate equation:

$$k_{\text{obs}} = k_{\text{OH}}[s]_0 + \varepsilon_1 \quad (9)$$

where, A is the measured absorbance of the transient, C is a fitting parameter, k_{obs} is the pseudo-first-order rate

constant, k_{OH} is the second-order bimolecular rate constant, and ε and ε_1 are error terms, which are normally distributed with mean 0 and variances σ^2 and σ_1^2 , respectively (i.e. $\varepsilon \sim N(0, \sigma^2)$, $\varepsilon_1 \sim N(0, \sigma_1^2)$). The model parameters C , σ^2 , σ_1^2 and k_{OH} were estimated simultaneously by a Markov Chain Monte Carlo (MCMC) simultaneous technique (40,000 simulations) using WinBUGS software (<http://www.mrc-bsu.cam.ac.uk/bugs>). For the pulse radiolysis experiments conducted using competition kinetics, the uncertainty in the second-order rate constant represents the standard error of the slope of the standard equation for competition kinetics (Buxton *et al.* 1988).

Figure 2 presents data for 2,4-DNT and 2,6-DNT obtained from the pulse radiolysis experiments. The pseudo-first-order rate constant was measured directly, and the linear dependence of k_{obs} on the initial concentration of the studied compound gives the absolute second-order hydroxyl radical rate constant.

k_{OH} rate constants values

A summary of the hydroxyl radical rate constants of the 10 CCL compounds is given in Table 2 and Figure 3, stating which oxidation method was used to generate the hydroxyl radicals (UV/H₂O₂ or pulse radiolysis). Also shown are values from the literature. In general, the values determined by the two methods would appear to agree quite well. However, for only two compounds, EPTC and terbacil, are

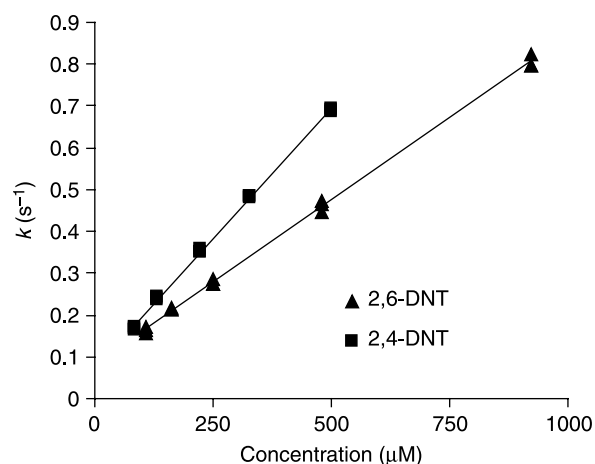


Figure 2 | Typical second-order rate constant determination using pulse radiolysis. Data shown is for 2,4-DNT and 2,6-DNT ($k_{\text{OH}} = (1.2 \pm 0.02) \times 10^9$ and $(0.8 \pm 0.01) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively).

Table 2 | k_{OH} values determined by UV/H₂O₂ and pulse radiolysis

Compound	k_{OH} (M ⁻¹ s ⁻¹)		Literature k_{OH} (M ⁻¹ s ⁻¹)
	UV/H ₂ O ₂	Pulse radiolysis	
2,6-dinitrotoluene	$(1.5 \pm 0.09) \times 10^{9*}$	$(0.78 \pm 0.01) \times 10^9$	0.75×10^9 Beltran <i>et al.</i> (1998)
2,4-dinitrotoluene	$(1.4 \pm 0.10) \times 10^{9†}$	$(1.2 \pm 0.02) \times 10^9$	–
EPTC	$(4.8 \pm 3.20) \times 10^{9†}$	$(4.5 \pm 0.20) \times 10^9$	–
Prometon	$(2.8 \pm 0.06) \times 10^{9*}$	$(3.5 \pm 0.07) \times 10^9$	–
Linuron	$(6.4 \pm 0.27) \times 10^{9*}$	$(5.0 \pm 0.13) \times 10^9$	4.3×10^9 De Laat <i>et al.</i> (1996) 5.6×10^9 Benitez <i>et al.</i> (2007)
Diuron	$(7.4 \pm 0.02) \times 10^{9*}$	$(6.5 \pm 0.09) \times 10^9$	4.6×10^9 De Laat <i>et al.</i> (1996) 7.1×10^9 Benitez <i>et al.</i> (2007)
RDX	$(1.1 \pm 0.07) \times 10^{9†}$	$(5.2 \pm 0.03) \times 10^{9‡}$	0.34×10^9 Bose <i>et al.</i> (1998)
Molinate	$(6.9 \pm 0.06) \times 10^{9†}$	$(3.7 \pm 0.02) \times 10^{9‡}$	0.85×10^9 Mabury & Crosby (1996) 2.14×10^9 Armbrust (2000)
Nitrobenzene	–	$(3.0 \pm 0.03) \times 10^9$ $(3.0 \pm 0.17) \times 10^9$	3.9×10^9 NDRL
Terbacil	$(7.4 \pm 0.69) \times 10^{9†}$	$(7.8 \pm 0.41) \times 10^9$	–

*molinate (6.9×10^9 M⁻¹s⁻¹, Shemer *et al.* 2006).

†nitrobenzene (3.9×10^9 M⁻¹s⁻¹, NDRL).

‡measured using competition kinetics with KSCN. All other pulse radiolysis values measured directly.

the values the same within 2-fold of their standard errors. A further comparison to the available values in the literature showed similar differences (with the exception of RDX and molinate, discussed below).

Within the scientific community investigating •OH radical rates with organic compounds, a factor of two is often considered as reasonable variation in terms of the absolute value of the second-order rate constant.

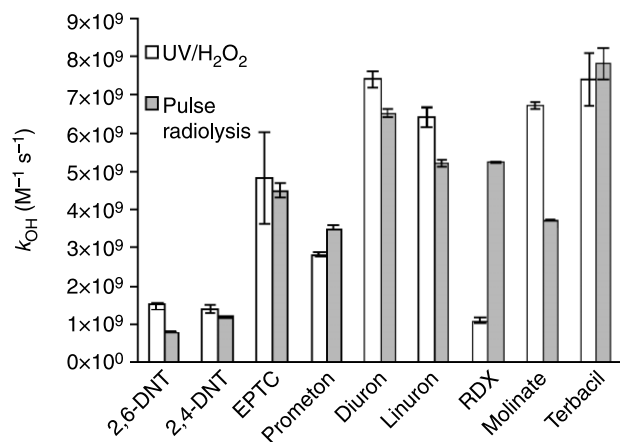


Figure 3 | Comparative k_{OH} (M⁻¹s⁻¹) values determined by UV/H₂O₂ and pulse radiolysis.

In particular, Haag & Yao (1992) suggested that a factor of two is often acceptable for the purposes of estimating oxidation rates during treatment processes. In their seminal compilation of •OH rate constants, Buxton *et al.* (1988) used the factor of two as a cut-off for whether or not it was appropriate to average two measured values from different studies.

Among the 9 compounds studied by UV/H₂O₂, only RDX showed higher variation (>2x) between k_{OH} values determined using UV/H₂O₂ and pulse radiolysis (Table 2). RDX and molinate also showed higher variation (15.4 and 4.5-fold, respectively) between the literature value and the pulse radiolysis value.

There are multiple sources of uncertainty in determination of k_{OH} values, including: the uncertainties in the experimental techniques; compounded error when Equation (7), or those associated with the pulse radiolysis experiments, are used; and uncertainty in the literature value for $k_{OH(ref)}$. In addition, when comparing values derived from different experimental studies, it is important to consider that the rate constants may also depend on the reaction conditions at which they were established such as pH and temperature. For the 10 compounds reported here,

none are ionizable at the circum-neutral pH values of interest. Hence, pH should not be a factor. With regard to temperature, Ashton *et al.* (1995) showed that k_{OH} of nitrobenzene increases with increased temperature ranging from 20 to 80°C. In the more relevant temperature range, assuming low activation energies (ca. 10 kJ mol⁻¹), a 3°C difference could affect a 5% difference in measured rates.

With regards to pulse radiolysis, despite this method being considered the most reliable, there are still potentially important sources of uncertainty or error in direct measurement and competition kinetics techniques that are not always easily recognizable from the kinetics (i.e. absorbance traces) alone (Buxton *et al.* 1988; Milosavljevic *et al.* 2005). In addition, when examining pulse radiolysis or gamma radiolysis values reported in the literature, it's important to note whether the system was saturated with N₂O, or the value was corrected for the potential for reaction between reducing species (H• and e_{aq}⁻) and the substrate (e.g. see Neta & Dorfman 1968).

For the UV/H₂O₂ experiments, there is potentially increased uncertainty for compounds that warrant the use of Equation (7). As mentioned earlier, the need to correct for loss of the substrate through direct photolysis was especially necessary for RDX EPTC and linuron. RDX, in particular, has a direct photolysis rate constant (k'_d) of $4.7 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$. The indirect photolysis rate of RDX using the UV/H₂O₂ system (with 25 mgL⁻¹ H₂O₂) was $5.6 \times 10^{-3} \text{ mJ}^{-1} \text{ cm}^2$. Hence, as much as 45% of RDX loss occurs through direct photolysis during UV/H₂O₂ experiment. It is possible that the difference between the k_{OH} of RDX determined from UV/H₂O₂ and pulse radiolysis is attributed to the fact that Equation (7) is over-correcting for the loss of RDX through direct photolysis.

Calculations that rely on competition kinetics also rely on accurate values of the reference compound. It is perhaps incautious to assume the explicit accuracy of values reported in the literature, or even the NDRL database. In a part of this study, UV/H₂O₂ experiments were performed using both molinate and nitrobenzene as reference compounds. The value determined for molinate ($6.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) using UV/H₂O₂ is 5 times higher than the previously published value of $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in the NDRL database. However, it should be noted that another publication by the same NDRL

cited authors reported a value of $8.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Mabury & Crosby 1996). Finally, the value measured using UV/H₂O₂ is 1.9 and 3.3 times larger than that obtained using pulse radiolysis ($3.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and reported by Armbrust (2000) ($2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Overall, this large range of values suggests considerable uncertainty in the true value.

Though the recommended NDRL value for the rate constant for •OH radical and nitrobenzene was used in these UV/H₂O₂ studies, we employed the pulse radiolysis method to reassess the NDRL value. The recommended value for nitrobenzene in the NDRL database is $3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, while two separate experiments from this study (conducted on different days with freshly made stock solutions) both provided values of $3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ though with different degrees of uncertainty. Using this value to analyze the UV/H₂O₂ competition kinetics (as opposed to the NDRL value) data would result in a decreased calculated k_{OH} value by a factor of 1.3.

Despite an abundance of published studies on reactions of hydroxyl radical with various pollutants, many of these studies examine removal efficiencies of a specific AOP set-up, and do not report intrinsic second-order rate constants. Hence, only a few of the 10 compounds reported in this study have published rate constants for reaction with hydroxyl radical. A rate constant of $7.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for 2,6-DNT was reported by Beltran *et al.* (1998) using a constant ozone concentration and excess hydrogen peroxide (0.05 M). A similar value was obtained in this research using pulse radiolysis. However, a higher value by factor of approximately two was determined using UV/H₂O₂.

A hydroxyl radical rate constant for linuron ($4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and diuron ($4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) was published by De Laat *et al.* (1996) using O₃/H₂O₂ process with atrazine ($1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) as a reference compound. However, if De Laat *et al.* had used an alternative value for the k_{OH} value of atrazine (e.g., $2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Haag & Yao 1992); $3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Acero *et al.* 2000); or $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (De Laat *et al.* 1994)), then their values would change appreciably and be closer to the values measured here by pulse radiolysis or the UV/H₂O₂ method. Benitez *et al.* (2007) published values of 5.6×10^9 and $7.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for linuron and diuron, respectively, using 4-chlorobenzoic acid as the reference compound in a photo-Fenton system. These values fall somewhat in

between the pulse radiolysis and UV/H₂O₂ values determined in this study.

For RDX, there was a significant difference in k_{OH} values obtained in this research compared to the published value of $3.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (Bose *et al.* 1998) which was estimated from pilot scale competition kinetic study with trinitrotoluene as a reference compound. There is no ready explanation for the discrepancy between these values.

The differences between the k_{OH} for nitrobenzene measured in this study and in the NDRL database were mentioned previously. Within the NDRL database, in addition to the recommended k_{OH} value of $3.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for nitrobenzene, there are four values with literature citations: 3.2, 3.5, 4.0, and $4.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. A review of the original publications showed that the Ashton *et al.* (1995) value of $4.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ was actually determined by normalizing their results to the NDRL recommended value of $3.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Although the normalization purportedly did not require more than 10% adjustment of the apparent value, the value cited in the NDRL database was not technically measured.

Both Fendler & Gasowski (1968) and Neta & Dorfman (1968) discussed the complications involved in monitoring the formation of the transient for nitrobenzene. Namely, there are possible complications in accounting for further reaction of the transient nitrobenzene radical via dimerization with longer reaction times. In light of this potential complication, the short response times ($< 10 \mu\text{s}$) used in the present study likely avoided these further reactions. Using competition kinetics in a gamma radiolysis system using ethanol as a reference compound, a method that may also avoid the complications of secondary reaction, Fendler & Gasowski (1968) reported a value of $2.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. (Note that this value is based on re-calculation of their data using the NDRL recommended $k_{OH/EtOH}$ value of $1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ rather than $1.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; i.e. the value used in the original publication). Though this value was not listed in the NDRL database, the study is referenced in the NDRL database for the value of a deuterated nitrobenzene, and it is quite close to the values measured in this study. In summary, despite our values being substantially different than the NDRL recommended value, closer examination of values in the NDRL database and other literature reports shows a considerably larger

range in values that perhaps challenges the notion that the NDRL recommended value is not without considerable uncertainty. The implications of having multiple, wide-ranging values for a bimolecular rate constant are discussed further below.

Practical implications for use of rate constants

One ultimate use of the rate constants measured in this and other studies is the prediction of pollutant degradation during an AOP. Assuming that only hydroxyl radical reactions contribute to the compound decay, the pollutant degradation kinetics can be described by the following equation:

$$-\frac{d[s]}{dt} = k_{OH(s)}[s][\bullet OH]_{ss} \quad (10)$$

Various methods exist for assessing the steady-state concentration of $\bullet OH$ radical depending on the type of AOP. For example, in the case of a LP UV/H₂O₂ system, the theoretical $[OH]_{ss}$ for 5 mg L⁻¹ of hydrogen peroxide is approximately $2.5 \times 10^{-15} \text{ M}$ (calculated using Equation (11)).

$$[\bullet OH]_{ss} = \frac{\sum_{\lambda} R_{OH}^{form}}{\sum_i R_{S,OH}[s]_i} = \frac{\sum_{\lambda} E_p^0(\lambda)(1 - \exp^{-2.303a(\lambda)z})f_{H_2O_2}}{\sum_i R_{S,OH}[s]_i} \quad (11)$$

Here, R_{OH}^{form} is the formation rate of hydroxyl radicals; $E_p^0(\lambda)$ is the incident UV photon flow ($\text{E L}^{-1} \text{ s}^{-1}$); $f_{H_2O_2}$ is the fraction of light absorbed by hydrogen peroxide; $R_{S,OH}^{form}[s]_i$ is the sum of the scavenging rate of hydroxyl radicals; $a(\lambda)$ is the solution absorbance (cm^{-1}); and z is the depth of solution (cm).

Dividing the time based rate (s^{-1}) obtained using Equation (10) by typical LP-UV average fluence rate (mW cm^{-2}) converts the time based rate constants into UV fluence based rate constants ($\text{mJ}^{-1} \text{ cm}^2$). The obtained UV fluence based rates were used to plot the theoretical decay

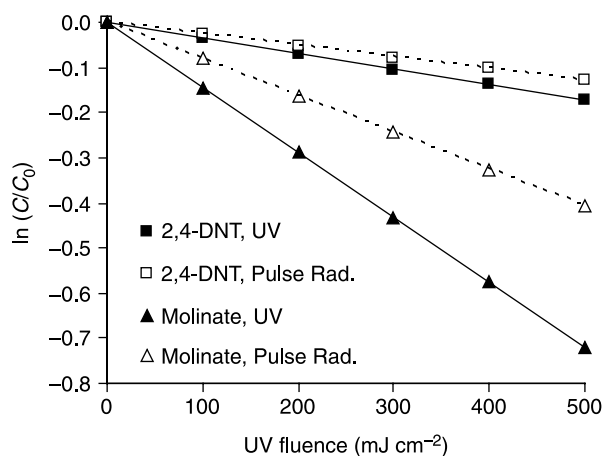


Figure 4 | The predicted decay of 2,4-DNT and molinate under UV/H₂O₂ oxidation. H₂O₂ concentration is 5 mg L⁻¹. Difference factors (between k_{OH} obtained using UV/H₂O₂ and pulse radiolysis) for these compounds are 1.3 and 1.9 respectively.

of various CCL compounds using k_{OH} values generated from both UV/H₂O₂ and pulse radiolysis in Figure 4.

As illustrated in Figure 4, even small differences in •OH rate constants can result in fairly large differences when trying to predict removals in an advanced oxidation process. For the UV-AOP example in Figure 4, there is only a small difference in the predicted removals of 2,4-DNT as the rate constants generated from the two methods differ by a factor of 1.1 of one another. Molinate •OH rate constants differ by a factor of 1.9, which for a UV dose of 500 mJ cm⁻² and an H₂O₂ concentration of 5 mg L⁻¹ (typical parameters for UV treatment of n-nitrosodimethylamine - NDMA) translates into either a 33% or 50% predicted removal if you use the pulse radiolysis or UV based rate constant respectively. Therefore, in the context of a near factor of two difference in rate constants, one observes approximately 20% variability in predicted contaminant removal. In cases where the reported rate constants differ as much as RDX (as compared to Bose *et al.* 1998) the differences clearly translate into much larger errors in the expected removals.

In the absence of a theoretical equation like Equation (11), the •OH radical exposure (or •OH radical CT) can be estimated by monitoring the loss of an easily measured probe or reference compound. Rearrangement of Equation (5) obtains

$$\ln \frac{[s]}{[s]_0} = \frac{k_{OH(s)}}{k_{OH(ref)}} \ln \frac{[ref]}{[ref]_0} \quad (12)$$

where the •OH radical exposure is defined as

$$\int [\bullet OH] dt = - \frac{1}{k_{OH(ref)}} \ln \frac{[ref]}{[ref]_0} \quad (13)$$

Using Equation (12), removal of a substrate, *s*, can be predicted by monitoring the removal of the reference compound, *ref*, once $k_{OH(s)}$ and $k_{OH(ref)}$ are known. This could be practical when the substrate is present at levels that make it difficult to monitor, or its analysis is extremely complicated or unfeasible, while the reference compound is more easily monitored. As mentioned above, one issue when using an equation such as Equation (12) is the compounding of uncertainty of the individual terms into the final prediction. In a theoretical exercise, we calculated the loss of the substrate as function of •OH radical exposure assuming $k_{OH(s)} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{OH(ref)} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 5). The value of $k_{OH(s)}$ was arbitrary but within the typical range of rate constants for organic pollutants, while the value of $k_{OH(ref)}$ was that of atrazine. An intriguing aspect of this calculation was the incorporation of uncertainty analysis in the predictions. Calculations were made assuming standard errors of 10, 20, and 30% of the means of normally distributed random variables $k_{OH(s)}$ and $k_{OH(ref)}$. From both a practical and potentially a regulatory point of view, we examined the predicted average (median) loss of the substrate as well as the predicted loss at the 90% lower (conservative) confidence limit (i.e. the conservative confidence bound). The analysis indicates

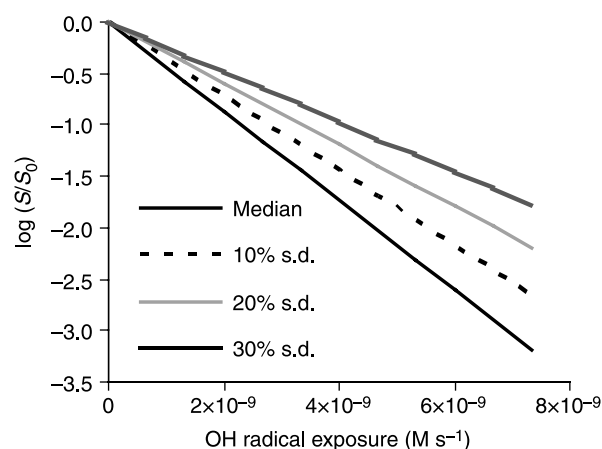


Figure 5 | Predicted loss of a micropollutant at the median and 90% confidence intervals assuming 10, 20, and 30% standard deviation in the rate constants.

that depending on the extent of compound removal, the differences in required $\bullet\text{OH}$ radical exposure between the median prediction and the 90% confidence interval can be dramatic. For example, to achieve a 1-log reduction of the substrate, median predicted removal requires an exposure of $2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ while the 90% CI requires $4.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ when the rate constants have 30% standard error. For 2-log removal, the values are $4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $8.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Hence, when there is only a 30% standard error in both rate constants, there is nearly a doubling of required $\bullet\text{OH}$ radical exposure necessary to achieve the same removal of the micropollutant when the system is operated within the 90% conservative confidence limit. These calculations could be extended to higher levels of uncertainty in the rate constants that are reflective of a factor of two between the rates reported in the literature.

Having multiple estimates for $\bullet\text{OH}$ radical rate constants can provide a means to measure uncertainty in these values, which is important if these contaminants are to be regulated in the near future and advanced oxidation processes are selected as a best available technology. With this information, supplemented by water quality data, predictions of contaminant removal can be made for different treatment scenarios and treatment technology based regulations could be implemented.

CONCLUSIONS

Of the 9 CCL compounds studied by UV/ H_2O_2 , only RDX showed greater variation than a factor of two between k_{OH} values determined using UV/ H_2O_2 and pulse radiolysis techniques. A factor of two is often considered as reasonable error in terms of the absolute value of hydroxyl radical second-order rate constant. Yet, theoretical calculation revealed that even small differences in k_{OH} rate constants values (<2) can result in fairly large differences (up to 50%) when trying to predict removal of pollutants in an advanced oxidation process. Availability of multiple reports for $\bullet\text{OH}$ radical rate constants may afford an important measure of uncertainty in these values, which is significant for predictions of contaminant removal for different treatment scenarios and treatment technology.

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