

## Relative reactivity of Contaminant Candidate List pesticides to OH radical oxidation

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Advanced oxidation processes (AOPs) represent those technologies that bring about enhanced oxidative degradation of pollutants in aqueous solution by the generation of hydroxyl radical ( $\cdot\text{OH}$ ). US Environmental Protection Agency (EPA) published, in February 2005, the second Contaminant Candidate List (CCL), which specifies 51 unregulated priority contaminants for the Agency's drinking water program. Various pesticides are included in the CCL since their extensive use worldwide was found to have serious environmental consequences with major impacts on water quality (Chiron et al., 2000). The purpose of the study was to determine kinetic rate constants of the chemical reactions resulting from the application of UV and UV/H<sub>2</sub>O<sub>2</sub> to the CCL pesticides: linuron (C<sub>9</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>), diuron (C<sub>9</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O), prometon (C<sub>10</sub>H<sub>19</sub>N<sub>5</sub>O), terbacil (C<sub>9</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>2</sub>), diazinon (C<sub>12</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub>PS), dyfonate (C<sub>10</sub>H<sub>15</sub>OPS<sub>2</sub>), terbufos (C<sub>9</sub>H<sub>21</sub>O<sub>2</sub>PS<sub>3</sub>), and disulfoton (C<sub>8</sub>H<sub>19</sub>O<sub>2</sub>PS<sub>3</sub>).

Batch kinetic experiments were conducted with either UV alone or in the presence of up to 100 mg/L H<sub>2</sub>O<sub>2</sub>. In quasi collimated beam experiments, 20 mM phosphate buffer solution at pH 7 of the studied pesticides, were exposed to average UV fluence (200-300 nm) levels between 0 and 600 mJ/cm<sup>2</sup>. Competition kinetics was used to evaluate the pesticides rate constants with hydroxyl radicals ( $k_{\text{OH}}$ ). In this method an organic substrate competes for hydroxyl radicals with a reference compound whose reactivity toward the hydroxyl radicals is known, under identical conditions (Einschlag et al., 2003).  $k_{\text{OH}}$  was evaluated using Eq. 1.

$$k_{\text{OH}} = \frac{k_s}{k_{\text{ref}}} \times k_{\text{OH}(\text{ref})} = \frac{\ln([s]/[s_0])}{\ln([\text{ref}]/[\text{ref}_0])} \times k_{\text{OH}(\text{ref})} \quad (1)$$

Where,  $k_s$  is the observed removal rate constant for the substrate, and  $k_{\text{ref}}$  is the observed, versus  $\ln([s]/[s_0])$  removal rate constant for the reference compound. A plot of  $k_s/k_{\text{ref}}$  gives a straight line passing through the origin and whose slope gives the  $\ln([\text{ref}]/[\text{ref}_0])$  ratio of rate constants  $k_s/k_{\text{ref}}$ . Molinate and nitrobenzene were chosen as reference compounds since their hydroxyl radical rate constants are well established (NDRL; Wink et al., 1991), and they essentially do not undergo significant direct photolysis.

The degradation of the studied pesticides by UV and UV/H<sub>2</sub>O<sub>2</sub> exhibited pseudo-first order reaction kinetics. In order to determine the effect of direct photolysis on  $k_{OH}$  determination in UV/H<sub>2</sub>O<sub>2</sub> systems, the direct photolysis rate constant was weighted by the ratio of the average irradiance with H<sub>2</sub>O<sub>2</sub> to that without H<sub>2</sub>O<sub>2</sub> and subtracted from the observed rate constant, which yielded a value for the indirect photolysis rate constant ( $k_i$ ), as shown in Eq. 2.

$$(2) \quad k_i = k_{obs} - \left[ \frac{E_{avg(H_2O_2)}}{E_{avg(w/o H_2O_2)}} \right] \times k_d$$

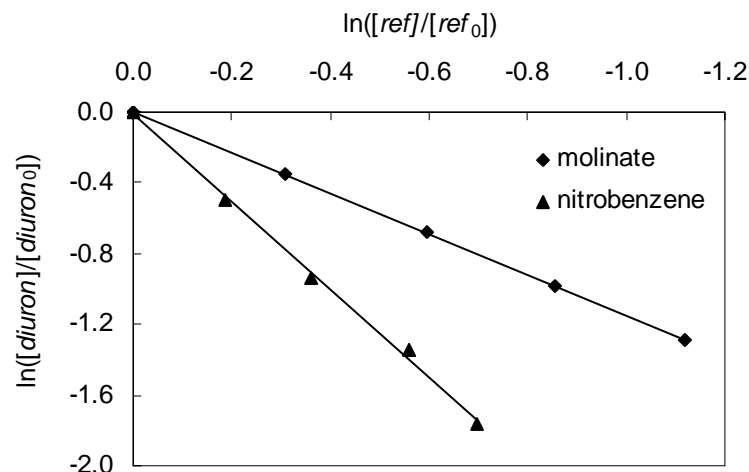
Where,  $k_d$  is the substrate direct photolysis rate constant;  $k_i$  is the indirect photolysis rate constant;  $k_{obs}$  is the overall removal rate constant using UV/H<sub>2</sub>O<sub>2</sub>;  $E_{avg(H_2O_2)}$  is the average irradiance with H<sub>2</sub>O<sub>2</sub>;  $E_{avg(w/o H_2O_2)}$  is the average irradiance without H<sub>2</sub>O<sub>2</sub>.

Once  $k_i$  was calculated for both the substrate and reference compounds,  $k_{OH}$  was estimated using Eq. 1. It was found that direct photolysis rate should be subtracted from the overall rate constant, as described by Eq. 2, when significant direct photolysis occurs or when photolysis is the main degradation mechanism of an organic compound. For all the pesticides, except of dyfonate, similar  $k_{OH}$  values were obtained using Eq. 1 and 2, as shown in Table 1 for prometon. Dyfonate showed high direct photolysis with rate constant of  $3.5 \times 10^{-3} \text{ mJ/cm}^2$ . Hence, its  $k_{OH}$  calculated using Eq. 1 was found to be 1.4 fold higher as compared to the value obtained using Eq. 2, for both reference compounds used, as illustrated in Table 1.

**Table 1.  $k_{OH} (\text{M}^{-1} \text{s}^{-1})$  values determined by UV/H<sub>2</sub>O<sub>2</sub> reaction.**

Compound	$k_{OH} (10^9 \text{ M}^{-1} \text{ s}^{-1})$			
	Eq. 1		Eq. 2	
	Molinate	Nitrobenzene	Molinate	Nitrobenzene
Prometon	0.5	2.5	0.5	2.7
Dyfonate	4.0	13.1	2.9	9.5

Figure 1 is a typical plot of a relative rate experiment of diuron using nitrobenzene and molinate as a reference compounds.



**Figure 1. Relative rate of diuron versus molinate and nitrobenzene using medium pressure UV lamp and 25 mg/L H<sub>2</sub>O<sub>2</sub>.**

As seen in Fig. 1, higher relative degradation of diuron was obtained using nitrobenzene as a reference compound as compared to molinate, which is reflected by the  $k_{OH}$  values of  $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $9.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  respectively. Higher  $k_{OH}$  values, by 4-7 fold, were determined using nitrobenzene as a reference compound as compared to molinate for the other pesticides studied. Although  $k_{OH}$  of nitrobenzene,  $3.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (NDRL) is only 3 times larger than the hydroxyl radical rate constant of molinate,  $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (NDRL).

The rate constants for the reaction of pesticides with the hydroxyl radicals ranged from  $0.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for prometon to  $4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for dyfonate, using molinate as a reference compound and from 2.5 to  $14.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for prometon and disulfoton respectively, using nitrobenzene as a reference compound. The small range in the rate constant values of the pesticides studied using the same reference compound, demonstrates the non-selective nature of hydroxyl radicals in aqueous solutions. However, the sensitivity of the rate constant measurement to the specific reference compound utilized must be recognized.

Among the pesticides studied disulfoton exhibited the highest rate constant, and prometon the lowest. These results can be explained by the complex methoxytriazine structure of prometon as compared to the aliphatic thiophosphate molecule of disulfoton. Generally, triazine oxidation is slow and cleavage of the triazine ring has yet to be reported (Watanabe et al., 2005). Linuron showed slightly slower reactivity toward hydroxyl radicals than diuron. Reactions of the urea moiety do not depend on the substituents on the aromatic ring, but rather on the substituents on the N atom. N-demethoxylation is reported to be more efficient than N-methyl oxidation or N-demethylation (Amine-Khodja et al., 2004). No significant effect was observed relative to the alkyl substitution in the lateral chains of disulfoton and terbufos as indicated by similar hydroxyl radical rate constants obtained.

Comprehensive understanding of the degradation kinetics of pesticides, listed as priority contaminants on the US EPA Contaminant Candidate List, using UV and UV/H<sub>2</sub>O<sub>2</sub> technology is fundamental to the regulatory future of these compounds as a part of the Agency's drinking water program.

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