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## Degradation of a Model Naphthenic Acid, Cyclohexanoic Acid, by Vacuum UV (172 nm) and UV (254 nm)/H<sub>2</sub>O<sub>2</sub>

Przemysław Drzewicz, Atefeh Afzal, Mohamed Gamal El-Din,\* and Jonathan W. Martin

*Department of Civil and Environmental Engineering, 3-133 Markin/CNRL Natural Resources Engineering Facility, University of Alberta, Edmonton, AB, T6G 2W2, Canada, and Department of Lab Medicine and Pathology, Division of Analytical and Environmental Toxicology, Faculty of Medicine and Dentistry, University of Alberta, Edmonton, AB, T6G 2G3, Canada*

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The mechanism of hydroxyl radical initiated degradation of a typical oil sands process water (OSPW) alicyclic carboxylic acid was studied using cyclohexanoic acid (CHA) as a model compound. By use of vacuum ultraviolet irradiation (VUV, 172 nm) and ultraviolet irradiation in the presence of hydrogen peroxide UV(254 nm)/H<sub>2</sub>O<sub>2</sub>, it was established that CHA undergoes degradation through a peroxy radical. In both processes the decay of the peroxy radical leads predominantly to the formation of 4-oxo-CHA, and minor amounts of hydroxy-CHA (detected only in UV/H<sub>2</sub>O<sub>2</sub>). In UV/H<sub>2</sub>O<sub>2</sub>, additional 4-oxo-CHA may also have been formed by direct reaction of the oxyl radical with H<sub>2</sub>O<sub>2</sub>. The oxyl radical can be formed during decay of the peroxy-CHA radical or reaction of hydroxy-CHA with hydroxyl radical. Oxo- and hydroxy-CHA further degraded to various dihydroxy-CHAs. Scission of the cyclohexane ring was also observed, on the basis of the observation of acyclic byproducts including heptadioic acid and various short-chain carboxylic acids. Overall, the hydroxyl radical induced degradation of CHA proceeded through several steps, involving more than one hydroxyl radical reaction, thus efficiency of the UV/H<sub>2</sub>O<sub>2</sub> reaction will depend on the rate of generation of hydroxyl radical throughout the process. In real applications to OSPW, concentrations of H<sub>2</sub>O<sub>2</sub> will need to be carefully optimized and the environmental fate and effects of the various degradation products of naphthenic acids considered.

### 1. Introduction

Canada's oil sands deposits represent one of the world's largest oil resources, representing an estimated 174 billion barrels of oil in form of bitumen.<sup>1</sup> For every barrel of oil produced by the oil sands surface mining industry, more than 2 barrels of fresh water are used to extract the bitumen using an alkaline hot water process.<sup>2</sup> The resulting oil sands process-affected water (OSPW) is recycled to reduce overall fresh water use, but the result is that OSPW becomes highly saline and acutely toxic to aquatic organisms, primarily due to high concentrations of naphthenic acids (NAs). NAs are a naturally occurring complex mixture of organic acids in bitumen and are largely composed of saturated alicyclic carboxylic acids.<sup>3</sup> They are persistent in OSPW, with overall degradation half-lives exceeding 13 years.<sup>4</sup> With an expanding oil sands industry in Northern Alberta, and increasing volumes of OSPW which must eventually be reclaimed, the effective remediation of OSPW has been a target of many studies since the 1980s.<sup>5</sup>

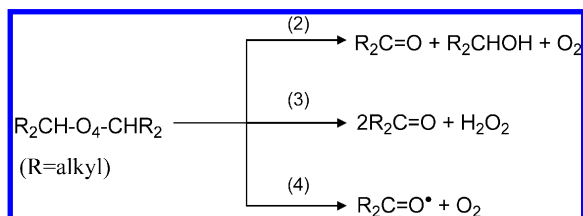
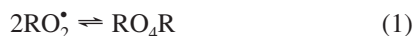
Naphthenic acids do not undergo significantly photolysis by direct ultraviolet (UV) or solar light due to low absorption.<sup>6,7</sup> In other produced waters, advanced oxidation processes (AOPs) have been extensively used for removal of refractory or toxic organic and inorganic pollutants, but to date the use of hydroxyl radical for treatment of OSPW has received little attention. In AOPs, hydroxyl radicals are generated in situ to react with organic compounds in an effort to produce less toxic, or less persistent, intermediates.

The mechanism of hydroxyl radical reaction with saturated alicyclic carboxylic acids (i.e., NAs) has not been examined, but the most common reaction of hydroxyl radical with saturated aliphatic carboxylic acids is hydrogen abstraction from the aliphatic chain.<sup>8</sup> On the basis of established reaction rate constants with aliphatic carboxylic acids in basic solution, it was observed that hydroxyl radical preferentially abstracts hydrogen from tertiary carbons, whereas the least reactive hydrogens toward hydroxyl radical are those on primary carbon atoms.<sup>8</sup> Under acidic conditions, the deactivating effect of the carboxylic acid group decreased from tertiary to primary carbon in  $\alpha$  position,<sup>9</sup> and saturated aliphatic carboxylic acids were oxidized principally at the  $\beta$ -carbon and the penultimate position. Comparatively, under basic conditions the carboxylate group increases the opportunity for delocalization of the unpaired electron, thus favoring abstraction of hydrogen from the  $\alpha$ -carbon due to resonance stabilization of the resulting  $\alpha$ -carbon centered radical, albeit oxidation of carboxylic acids at the penultimate position was also observed under basic conditions as well; however, the oxidation at the penultimate position may have been induced by the TiCl<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system used for generation of hydroxyl radical.<sup>9</sup>

Although there is no information about hydroxyl radical degradation of alicyclic carboxylic acids to date, the mechanisms of degradation of other organic compound by hydroxyl radical in aqueous solution may be relevant to the mechanism of decomposition. The general mechanism of hydroxyl radical induced degradation of organic compounds was proposed by von Sonntag and Schuchmann.<sup>10</sup> Generally, the hydroxyl radicals react with an organic compound to produce an organic radical which, in turn, reacts with molecular oxygen to form a peroxy

\* To whom correspondence should be addressed. Phone: (780) 492-5124. Fax: (780) 492-8198. E-mail: mgamalel-din@ualberta.ca.

radical. Oxygen is normally present in solution when advanced oxidation processes such as ultraviolet irradiation in presence of hydrogen peroxide (UV/H<sub>2</sub>O<sub>2</sub>), ozonation (O<sub>3</sub>), Fenton processes (Fe(II)/H<sub>2</sub>O<sub>2</sub>), or their combination are applied for decomposition of organic pollutants. Peroxyl radicals may combine, forming short-lived tetroxide species (reaction 1) which decomposes via a number of pathways (reactions 2–4)<sup>10</sup>



The exact mechanism of these reactions is still controversial. There is a dispute concerning whether the product-forming process is sequential or concerted; however, the occurrence of the reactions and formation of these products was reported by many authors.<sup>10</sup>

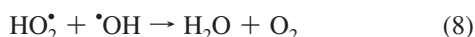
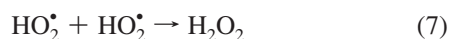
In most studies on hydroxyl radical induced degradation of organic compounds, reviewed by von Sontang and Schuchmann,<sup>10</sup> radiolysis of water is used as a source of hydroxyl radical. However, photolysis of water with light below 190 nm can be also used as a convenient source of hydroxyl radical<sup>11</sup> because the UV absorption of water steadily increases from approximately 190 to 120 nm,<sup>12</sup> and its electronic excitation leads to its photolysis with the production of hydrogen atoms and hydroxyl radicals



The Xe-excimer lamp emission domain is  $172 \pm 14$  nm.<sup>13</sup> At 172 nm, the quantum yield for production of hydroxyl radical is  $\Phi_{\text{HO}^{\bullet}} = 0.42$ ;<sup>13</sup> the quantum yield for the production of hydrated electrons is lower than 0.05. Hydrogen atoms can be quenched by molecular oxygen which is not reactive toward hydroxyl radical<sup>9</sup>

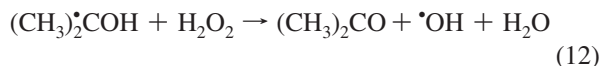
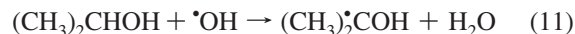


The formed perhydroxyl radicals (HO<sub>2</sub><sup>•</sup>) are much less reactive toward organic compounds than hydroxyl radical and can decay by a recombination reaction to form hydrogen peroxide (reaction 7) or water and oxygen (reaction 8)<sup>14</sup>



In vacuum UV (VUV) photolysis of water, H<sub>2</sub>O<sub>2</sub> concentrations may build-up with very long irradiation times (reaction 7),<sup>14,15</sup> or by decomposition of organic peroxyl radicals (reaction 3).<sup>10,16</sup> However, the concentration of formed hydrogen peroxide in these cases is very low and will generally not interfere in the reaction process.

It is well known that H<sub>2</sub>O<sub>2</sub> may react with organic radicals, inducing secondary reactions.<sup>17</sup> For example, for 2-propanol it was found that the intermediate organic radicals reacted with hydrogen peroxide to form acetone<sup>18</sup>



Hydroxyl radicals are also generated by UV irradiation of H<sub>2</sub>O<sub>2</sub>. In the UV/H<sub>2</sub>O<sub>2</sub> processes, H<sub>2</sub>O<sub>2</sub> is added in excess to generate hydroxyl radicals over the entire process time.<sup>19</sup> The high concentrations of H<sub>2</sub>O<sub>2</sub> in the UV/H<sub>2</sub>O<sub>2</sub> process are more likely to play important roles in the decomposition of organic compounds and affect formation of byproduct than in the VUV process.

In this study, cyclohexanoic acid (CHA) was selected as a simple model NA compound. Although there are relatively few NAs with less than 9 carbons in OSPW, NAs containing one ring are a prominent class. The degradation of CHA was studied by VUV and UV/H<sub>2</sub>O<sub>2</sub>. This allowed the mechanism of hydroxyl radical induced decomposition of CHA to be investigated, based on identification of formed byproduct in both systems, and the possible role of H<sub>2</sub>O<sub>2</sub> in the decomposition mechanism was evaluated by comparing byproducts and reaction rate constants in the two systems.

## 2. Experimental Section

**2.1. Materials.** CHA, *cis*-4-hydroxycyclohexanoic acid (*cis*-4-hydroxy-CHA), and *trans*-4-hydroxycyclohexanoic acid (*trans*-4-hydroxy-CHA) were of analytical grade purity (99+%) and were purchased from TCI (Portland, OR, USA). All analyte solutions were prepared in ultrapure water (resistivity = 18 MΩ × cm and TOC < 0.1 mg/L) prepared with a Millipore RO-Milli-Q system equipped with a UV lamp, adjusted to pH 9 with carbonate free 50% sodium hydroxide (ACS purity). Hydrogen peroxide (ACS purity, Fisher Scientific Co., Canada) solutions were prepared from 30% w/w stock solution. Ammonium acetate and methanol were purchased from Fisher Scientific (LC-MS grade).

**2.2. VUV Irradiation.** A dielectric barrier discharge Xe<sub>2</sub><sup>+</sup> excilamp (Model BD-P-barrier discharge portable, Institute of High Current Electronics, Tomsk, Russia<sup>20</sup>) with dimensions 26.5 × 7.7 × 77 cm (length × width × height) including a cooling fan was used for the VUV study. The lamp was placed in a collimated beam apparatus designed specifically for VUV experiments.<sup>21</sup> During irradiation, the lamp was cooled with gaseous nitrogen (100 mL/min), also functioning to prevent formation of ozone from photolytic excited oxygen.<sup>10</sup> Because of low penetration of 172 nm light emitted by the lamp (less than 70 μm in water<sup>22</sup>), the reactor was a 3 mL Suprasil quartz cuvette with a stopper and a small magnetic stir bar. An actinometry method, using methanol, was employed for calculating the fluence rate (irradiance) of the xenon excilamp at 172 nm<sup>23</sup> to be  $0.67 \pm 5\%$  mW/cm<sup>2</sup>, and the yield of <sup>•</sup>OH was  $1.4 \times 10^{-9}$  mol s<sup>-1</sup> ( $\Phi = 0.42$ , photon flow =  $3.34 \times 10^{-9}$  mol s<sup>-1</sup>).<sup>21</sup> The naturally dissolved oxygen was not removed from solutions because oxygen quenched the formation of H<sup>•</sup>. Contrary to γ-radiolysis, N<sub>2</sub>O cannot be added to scavenge H<sup>•</sup> in a VUV system because N<sub>2</sub>O undergoes photolysis to N<sub>2</sub> and singlet oxygen.<sup>24,25</sup>

**2.3. UV Irradiation in Presence of H<sub>2</sub>O<sub>2</sub>.** The UV/H<sub>2</sub>O<sub>2</sub> experiments were carried out using a collimated beam apparatus from Calgon Carbon Corporation (Pittsburgh, PA, USA). A 10-W low pressure UV lamp (Calgon Carbon, Pittsburgh, PA, USA) was used for the UV/H<sub>2</sub>O<sub>2</sub> experiments. The main light emission of the low pressure lamp is at 254 nm. A radiometer (International Light Inc. Model IL 1400A) equipped with a UV detector (International Light Inc. Model SED240) and a neutral density filter (Model QNDS2), calibrated at 5 nm intervals in the range of 200–400 nm, was used to measure the irradiance at the surface of the water samples. The average fluence rate in the solution and the delivered fluence (UV dose) were calculated based on the Bolton and Linden protocol<sup>26</sup> and the spreadsheets available at [www.iuva.org](http://www.iuva.org) for low pressure UV lamps for shallow (<2 cm) solutions. The fluence rate of the lamp was calculated to be 13.69 mW/cm<sup>2</sup> and the yield of <sup>•</sup>OH generation  $8.2 \times 10^{-6} \text{ mol s}^{-1}$  ( $\Phi = 1$ , Petri dish area = 28.26 cm<sup>2</sup>, radiant energy of 1 mol of 254 nm photon = 470.971 kJ mol<sup>-1</sup>).

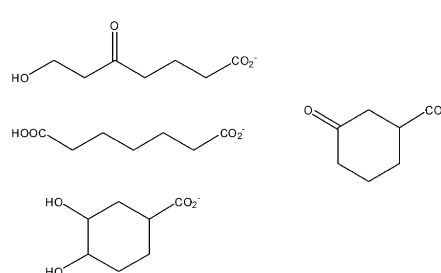
**2.4. Analytical Methods.** The analytical method was designed for separation of CHA and two hypothesized degradation products, *cis*-4- and *trans*-4-hydroxycyclohexanoic acid. Analytical high-performance liquid chromatography (HPLC) columns (Luna C8, 5  $\mu\text{m}$ , 150  $\times$  3 mm, and 250  $\times$  3 mm; Phenomenex) were used for reversed-phase chromatography. For routine analysis, an HPLC coupled to an ion trap mass spectrometer (Varian 500-MS) with unit mass resolution was used. For confirmation of empirical formulas, an HPLC coupled with a time-of-flight mass spectrometer (Agilent 6220, 10,000 mass resolution) was used. Both mass spectrometers were equipped with an electrospray interface operating in negative ion mode. Chromatography was performed at 40 °C at a flow rate 200  $\mu\text{L}/\text{min}$ , and injection volumes were 20  $\mu\text{L}$ . The mobile phase consisted of 100% methanol and 4 mM ammonium acetate with 0.1% acetic acid in aqueous solution. The concentration of methanol was ramped from 40 to 80% over 20 min. Chromatograms of carboxylic acid standards showed that retention times were generally in order of decreasing polarity. To achieve better resolution of more polar byproduct and their isomers, a longer column (250 mm, otherwise identical to above) was also applied. The same mobile phases were used, but the initial concentration of methanol was 30%, and after 10 min it was slowly ramped to 70% over 30 min. Heptanoic and octanoic acid both eluted after 80 min; thus 80 min was the total run time.

Ion chromatography with conductivity detection was used to detect any short-chain carboxylic acids. Chromatography was performed at 40 °C and injection volumes were 200  $\mu\text{L}$ . The mobile phase consisted sodium hydroxide solution at flow rate 1 mL/min. The concentration of NaOH was ramped from 2.5 to 5 mM over 15 min and then from 5 mM to 38.25 mM. The electrochemical suppressor current was 100 mA. The AS11-HC (4 mm  $\times$  250 mm) with a guard column AG-11 was used (Dionex, Sunnyvale, CA, USA). To remove carbonate residue from the eluent, an anion trap column (ATC-HC, Dionex, Sunnyvale, CA, USA) was used.

### 3. Decomposition of CHA by VUV

The study of hydroxyl radical decomposition of organic compounds using VUV must be conducted at relatively low concentration. This is because, at high concentration, direct photolysis of organic compounds can interfere.<sup>6</sup> To ensure that direct photolysis of CHA was not occurring in the range

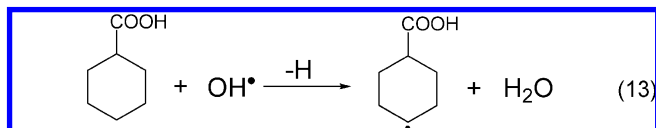
**TABLE 1: Chemical Formulae and Proposed Structure(s) of Major By-Products Formed by VUV and UV/H<sub>2</sub>O<sub>2</sub> at *m/z* 141 and 159**

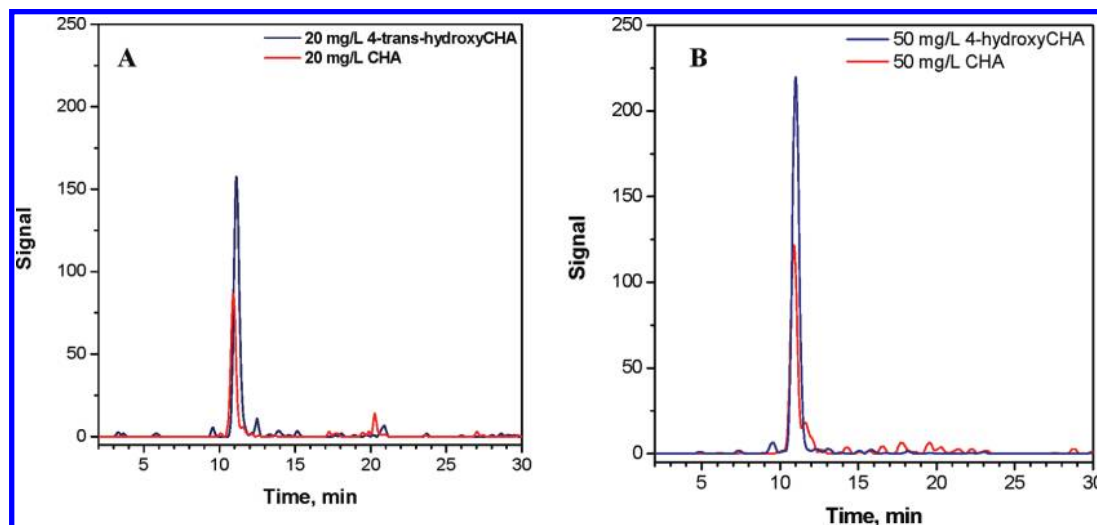
	By-product(s) 1	By-product(s) 2
Mass Detected ( <i>m/z</i> )	159.0737	141.06287
Empirical Formula	C <sub>7</sub> H <sub>11</sub> O <sub>4</sub> <sup>-</sup>	C <sub>7</sub> H <sub>9</sub> O <sub>3</sub> <sup>-</sup>
Calculated Mass ( <i>m/z</i> )	159.0736	141.06299
Mass Error	-0.6 ppm	-0.84 ppm
Proposed Structure(s)		

of concentrations used here, the kinetics of degradation were examined. Direct photolysis follows zero-order kinetics, whereas degradation processes based on generation of hydroxyl radical should follow pseudofirst order kinetics.<sup>11,14,24</sup> It was determined that at up to 20 mg/L of CHA (highest concentration used in the experiments) in aerated aqueous solutions, the degradation followed pseudo-first-order kinetic decay. Under these conditions, the hydroxyl radicals are present in solution in excess, and the process is independent of the rate of <sup>•</sup>OH generation from photolysis of water. Furthermore, we observed that the addition of 80  $\mu\text{M}$  *tert*-butanol, a hydroxyl radical scavenger, significantly decreased the effectiveness of CHA decomposition (40  $\mu\text{M}$ ). Taken together, these results indicated that decomposition of CHA in the investigated range was induced primarily by <sup>•</sup>OH.

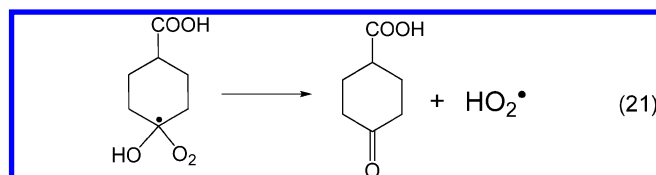
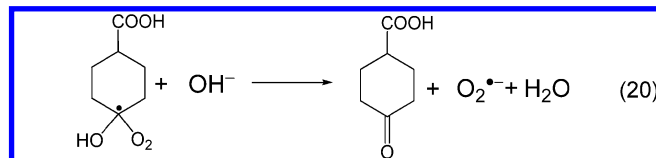
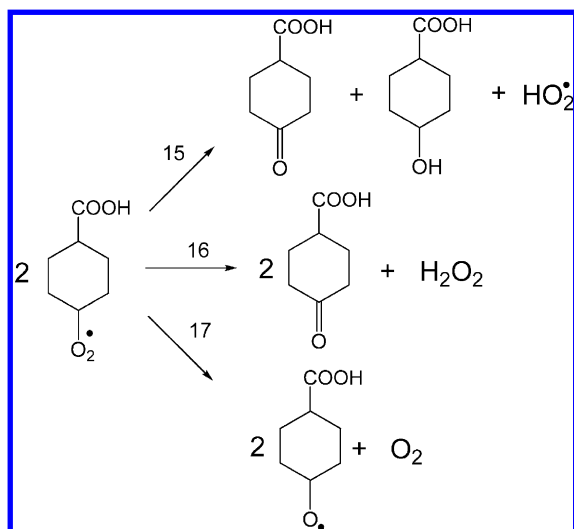
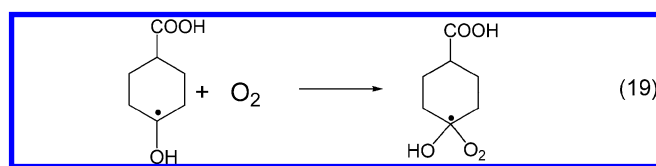
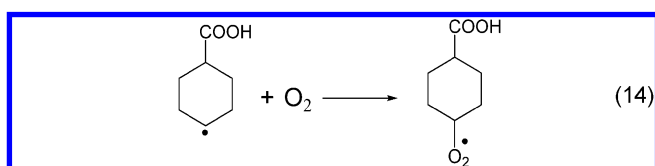
At an initial concentration of 20 mg/L CHA, 90% degradation was achieved after 15 total minutes of irradiation. In a study of the reaction products, HPLC high resolution mass spectrometry indicated two major byproduct at *m/z* = 159.0737 and 141.06287 (the calculated *m/z* of CHA is 128.1690) (Table 1). These same products were also found using the ion trap in autoscanning MS/MS mode, and we examined the product ions of *m/z* = 159.0737 and 141.06287 for structural elucidation, but the *m/z* 159 signal intensity was too low to collect MS/MS spectra. However, retention times of the *m/z* 159 degradation products identified here were the same as those observed during UV/H<sub>2</sub>O<sub>2</sub>; thus MS/MS spectra of *m/z* 159 were collected on the UV/H<sub>2</sub>O<sub>2</sub> samples (discussed in the next section).

The ion at *m/z* = 141.06287 is characteristic of an oxo-cyclohexanoic acid (oxo-CHA, Table 1), and in MS/MS the product ion at *m/z* = 97, representing a neutral loss of 44, suggested the presence of a carboxylate group (Figure 1). The formation of such a product suggested that after hydrogen abstraction by hydroxyl radical (reaction 13) the resulting radical reacted with oxygen to form peroxy-CHA radical (reaction 14) which may subsequently decay by recombination reactions (reactions 15–17).

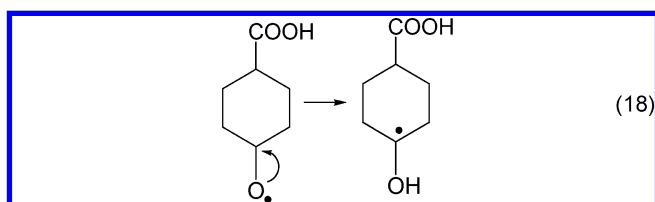




**Figure 1.** Confirmed formation of 4-oxo-CHA (A) after 5 min VUV treatment and (B) after 60 min UV/H<sub>2</sub>O<sub>2</sub> treatment of (red line) CHA and (blue line) *trans*-4-hydroxyCHA, respectively. Chromatograms are for MS/MS transition *m/z* 141/97, characteristic of neutral loss of CO<sub>2</sub> from 4-oxo-CHA.



The possible radical product formed in reaction 17 may have undergone further peroxidation as the oxyl radical can undergo  $\alpha$  hydrogen shift (reaction 18) and then react with oxygen to form a peroxy radical (reaction 19), which could decompose to oxo-CHA (reaction 20) as observed in the analogous decomposition of secondary alcohols.<sup>27</sup> The decay of this peroxy radical may also be induced by hydroxide anion (reaction 21)<sup>27</sup>



Our further study of the VUV-induced degradation of *trans*-4-hydroxy-CHA also showed formation of a byproduct at *m/z* 141 (Figure 1). In fact, this byproduct eluted at the same retention time as the aforementioned oxo-CHA byproduct of CHA degradation and produced the same *m/z* 97 product ion in MS/MS. Therefore, both CHA and *trans*-4-hydroxy-CHA produced a major oxo-CHA byproduct, and it is likely that the VUV CHA byproduct was also 4-oxo-CHA. *trans*-4-Hydroxy-CHA was likely decomposed to oxo-CHA through reactions 19–21. Therefore, it is also likely that any 4-hydroxy-CHA produced from CHA (i.e., as in reaction 15) would have been subsequently converted to 4-oxo-CHA. The rate constants of reaction for *cis*- and *trans*-4-hydroxy-CHA with hydroxyl radical (Table 2) are comparable to the literature rate constant of CHA ( $k = 5.5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  at pH 9<sup>8</sup>). It is also notable that there was a statistically significant difference between the hydroxyl radical rate constants of *cis*- and *trans*-4-hydroxy-CHA. Unlike 4-oxo-CHA, which can be formed by all three proposed degradation pathways of the peroxy-CHA radical (reactions 15–17), hydroxy-CHA can only be formed in (reaction 15). Taken together, this may explain no detectable yield of hydroxy-CHA from CHA and in these VUV experiments.



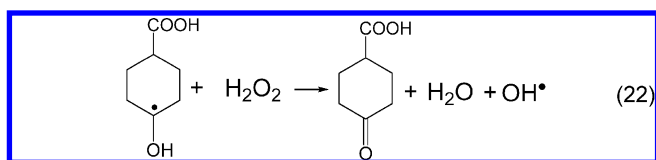
**TABLE 2: Comparison of Rate Constants Measured in VUV and UV/H<sub>2</sub>O<sub>2</sub> at pH 9 Using Competitive Kinetics and Cyclohexanoic Acid as the Reference ( $k = 5.5 \times 10^9 \text{ (L mol}^{-1} \text{ s}^{-1})^3$ )**

compound	rate constant ( $\text{L mol}^{-1} \text{ s}^{-1}$ ), $n = 3$	
	VUV	UV/H <sub>2</sub> O <sub>2</sub>
4- <i>trans</i> -hydroxycyclohexanoic acid	$5.5 \pm (0.03) \times 10^9$	$2.4 \pm (0.42) \times 10^9$
4- <i>cis</i> -hydroxycyclohexanoic acid	$4.1 \pm (0.12) \times 10^9$	$3.5 \pm (0.35) \times 10^9$

### 5. Decomposition of CHA by UV/H<sub>2</sub>O<sub>2</sub>

The efficiency of the UV/H<sub>2</sub>O<sub>2</sub> process depends on the concentration of hydrogen peroxide, and two hydroxyl radicals are formed during photolysis of H<sub>2</sub>O<sub>2</sub>.<sup>11</sup> However, because of the reaction of the produced hydroxyl radicals with H<sub>2</sub>O<sub>2</sub>, the effective amount of hydroxyl radicals produced in the process is lower than predicted by simple photolysis of H<sub>2</sub>O<sub>2</sub>.<sup>28</sup> Additionally, H<sub>2</sub>O<sub>2</sub> may also react directly with organic byproduct, thus further decreasing the efficiency of hydroxyl radical formation in the processes.<sup>17,29</sup> Thus, it is necessary to optimize the added amount of H<sub>2</sub>O<sub>2</sub> in each application. In our system, the highest efficiency of CHA degradation was obtained when the molar ratio of H<sub>2</sub>O<sub>2</sub>:CHA was 23. The optimum ratio was consistent for 1, 10, and 80 mg/L of CHA. It was also confirmed in control experiments that CHA and hydroxy-CHA did not react directly with H<sub>2</sub>O<sub>2</sub>. Furthermore, the absorption spectra of these compounds showed absorption only below 210 nm, and compounds did not undergo photolysis at 254 nm.

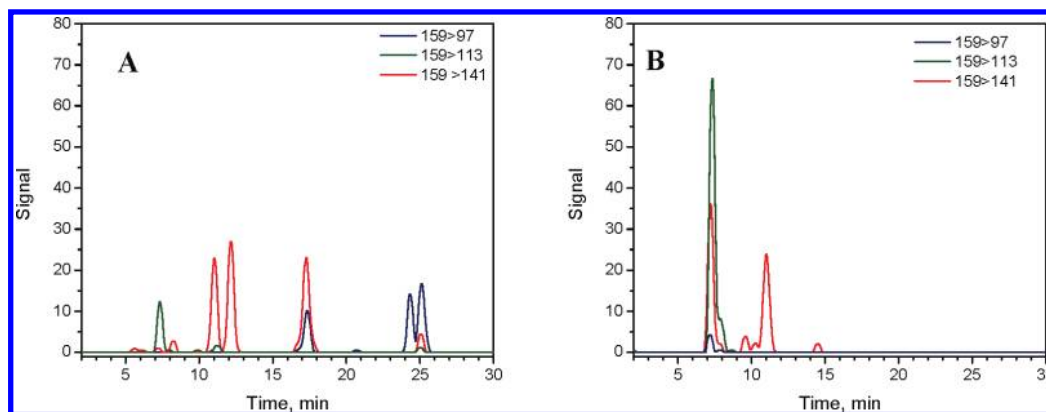
Despite a higher rate of formation of hydroxyl radicals than in VUV, 90% degradation of 20 mg/L CHA by UV/H<sub>2</sub>O<sub>2</sub> was only achieved after 80 min of treatment. The main byproduct, as in VUV, appeared to be 4-oxo-CHA based on retention time and MS/MS product ions (Figure 1). In the UV/H<sub>2</sub>O<sub>2</sub> process, 4-oxo-CHA may be formed in reactions of H<sub>2</sub>O<sub>2</sub> with organic radicals. The oxyl radical of CHA formed in reactions 17 and 18 may react with H<sub>2</sub>O<sub>2</sub> (reaction 22), as was observed in the UV/H<sub>2</sub>O<sub>2</sub> oxidation of 2-propanol<sup>18</sup>



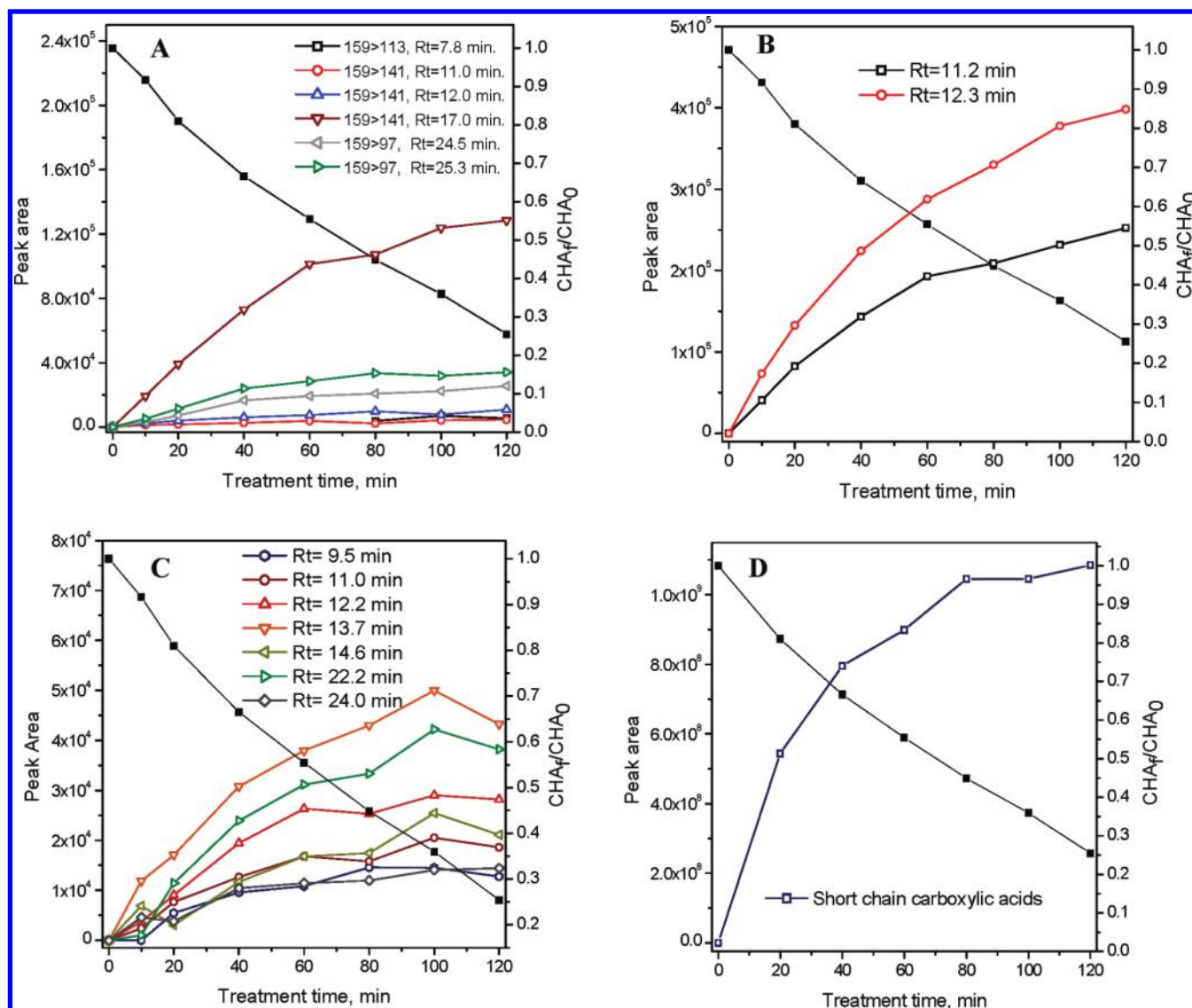
Study of the decomposition of 20 mg/L *trans*-4-hydroxy-CHA by UV/H<sub>2</sub>O<sub>2</sub> also showed formation of 4-oxo-CHA during the process (Figure 1). This indicated that hydroxy-CHAs that may

be formed during CHA degradation by UV/H<sub>2</sub>O<sub>2</sub> could also undergo degradation in a mechanism involving reaction with H<sub>2</sub>O<sub>2</sub> (reaction 22). As in VUV, this may be a reason for no detectable yield of hydroxy-CHA by UV/H<sub>2</sub>O<sub>2</sub>. Additionally, our relative rate measurements showed that apparent rate constants for the reaction of 4-hydroxy CHAs (*cis* and *trans*) with hydroxyl radical were lower than those measured by VUV (Table 2), thus indicating that H<sub>2</sub>O<sub>2</sub> may play a role in the decomposition mechanism of CHA at the concentrations employed here. This is because the direct reaction of H<sub>2</sub>O<sub>2</sub> with organic compound decreases the number of hydroxyl radicals generated in the UV/H<sub>2</sub>O<sub>2</sub> process. It is germane to note that, as was the case in VUV, there was a statistically significant difference between the degradation rate constants for *cis*- and *trans*-4-hydroxy-CHA by UV/H<sub>2</sub>O<sub>2</sub> (Table 2).

At 20 mg/L of CHA or *trans*-4-hydroxy-CHA, no other products (other than 4-oxo-CHA) were observed; thus a 50 mg/L initial CHA concentration was used for product analysis, and several byproducts were identified by MS/MS at  $m/z$  159. These were assigned as isomers of dihydroxy-CHA due to characteristic  $m/z$  97 and 141 product ions (Figure 2). The 97  $m/z$  product ion (neutral loss of 62, dihydroxyethane) may indicate compounds containing vicinal hydroxyl groups or two hydroxyl groups on the same carbon. Those products could be formed by addition of hydroxyl radical to the hydroxy-CHA radical formed in reaction 18 or addition of hydroxyl radical to the double bond of enol tautomers of 4-oxo-CHA. The  $m/z$  141 product (indicating neutral loss of 18, or H<sub>2</sub>O) may indicate compounds containing one or more isolated hydroxyl groups. Neutral loss of 18 was also observed in the MS/MS spectra of our 4-hydroxy-CHA standards ( $m/z$  143 > 125 transition). The structure of the various dihydroxy-CHA isomers may be elucidated, in part, by retention time. On the basis of analogy to dihydroxybenzoic acids isomers separated by reverse-phase chromatography,<sup>30</sup> it is suggested that less polar dihydroxycyclohexanoic acids containing vicinal hydroxyl groups eluted later than other dihydroxy isomers.

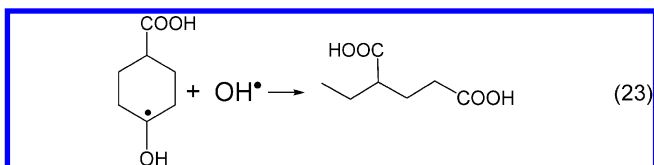


**Figure 2.** Chromatograms confirming formation of byproduct with  $m/z$  159 during UV/H<sub>2</sub>O<sub>2</sub> decomposition of (A) 50 mg/L CHA and (B) 50 mg/L 4-*trans*-hydroxy CHA after 60 min. Transition 159 > 113 is characteristic of heptadiic acids, and transitions 159 > 141 and 159 > 97 are characteristic of dihydroxy CHAs.



**Figure 3.** UV/H<sub>2</sub>O<sub>2</sub> degradation of 50 mg/L CHA (right axis, relative units, marked as ■) and formation of byproduct (left axis, peak area units): (A) dihydroxy-CHAs and heptadioic acid, (B) oxo-CHAs, (C) hydroxy-CHAs, (D) total short-chain carboxylic acids by ion chromatography.

The  $m/z$  159 > 113 transition in treated CHA chromatograms indicated neutral loss of 46 (formic acid), which may also suggest the presence of heptadioic acids as products. A proposed explanation for formation of heptadioic acid may be reaction of the oxyl radical with hydroxyl radical (reaction 23). The formation of  $m/z$  159 products over the process time is presented in Figure 3.

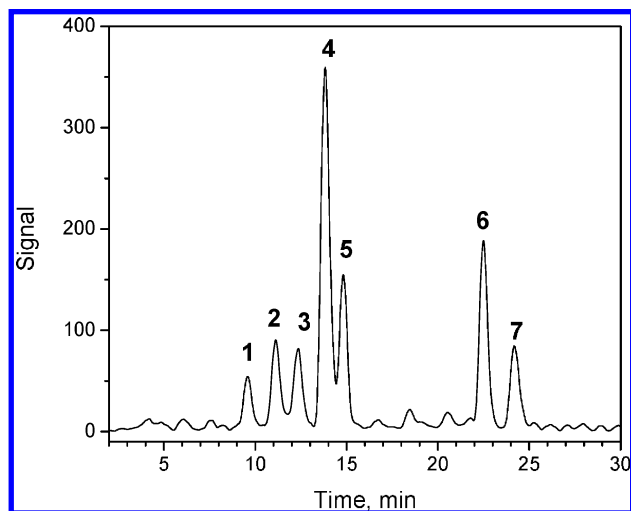


Other hydroxy-CHA isomers (i.e., other than 4-hydroxy CHA) were also identified among the products of 50 mg/L CHA after 80 min of treatment. This was based on products with an  $m/z$  143 > 125 transition (i.e., neutral loss of 18 or H<sub>2</sub>O). Seven total hydroxy-CHA isomers were observed, corresponding to all the possible isomers (1-hydroxy, and the *cis* and *trans* isomers of 2, 3, and 4-hydroxy-CHA), but position 4 was the most preferable based on peak area of peak 1 and 4 (*trans*- and

*cis*-4-hydroxycyclohexanoic acid, respectively, Figure 4). The production of these hydroxy-CHA products over the process time is presented in Figure 3.

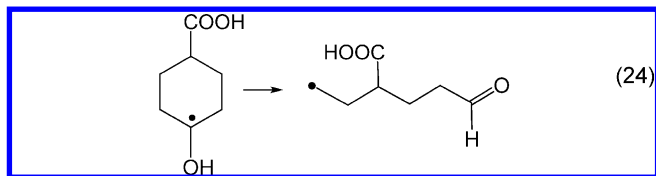
Formation of byproduct at  $m/z$  159 was also observed in the decomposition of 4-hydroxy-CHA. The  $m/z$  159 > 141 transition and neutral loss of 18 was characteristic of the aforementioned dihydroxy-CHA isomers observed in the degradation of CHA. However, unlike with CHA, here there were no dihydroxy isomers at later retention times having the  $m/z$  159 > 97 transition, characteristic of vicinal dihydroxy-CHA isomers. This indicates that one of the pathways for degradation of 4-hydroxy-CHA is hydroxylation of the hexane ring, presumably at carbon position 1 or 2. Additionally, the early eluting compound having the  $m/z$  159 > 113 transition was found at the same retention time here as in CHA degradation experiments, likely isomers of heptadioic acid formed through reaction 23.

The formation of short-chain aliphatic carboxylic acids containing from one to four carbons was observed by ion chromatography. These could not be clearly resolved under the chromatographic conditions, and complex chromatograms were resultant, likely representing coeluting short-chain acids with their respective oxo- or hydroxy- derivatives. The concentration



**Figure 4.** Formation of hydroxy-CHA isomers during UV/H<sub>2</sub>O<sub>2</sub> decomposition of 50 mg/L CHA. Chromatogram is for MS/MS transition *m/z* 143. Peaks 1 and 4 are *trans*- and *cis*-4-hydroxy-CHA, respectively.

of total short-chain aliphatic carboxylic acids (measured as summary area of peaks) was increasing over the process time process (Figure 3). These short-chain byproducts may be formed from an initial reaction involving  $\beta$ -scission of the oxyl radical (reaction 24).<sup>9</sup> One can be assumed that formed radical in this reaction is very unstable and quickly undergo degradation.

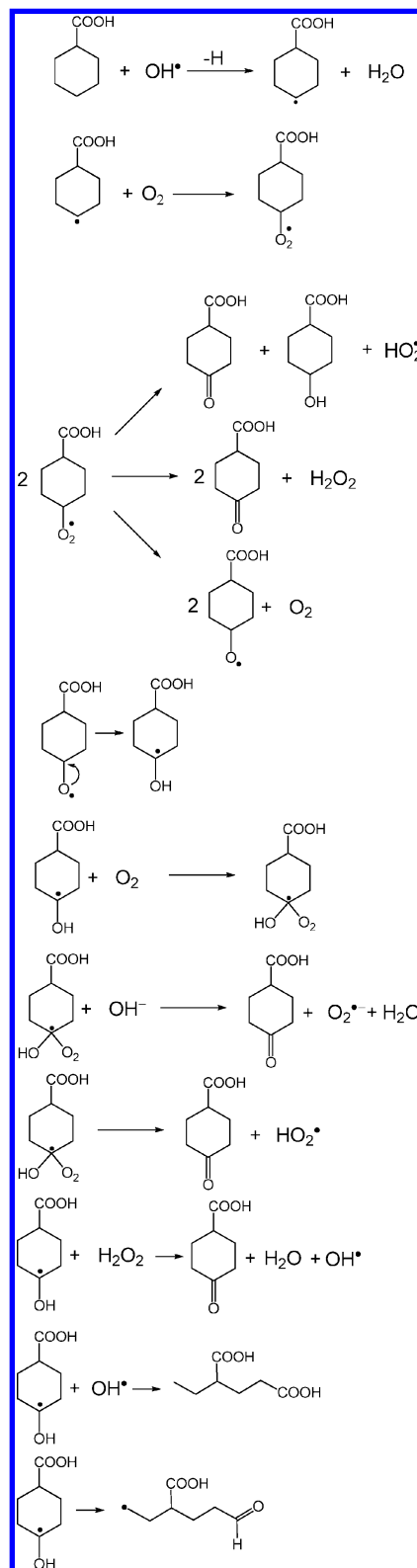


Formation of hydroxyl-CHA and oxo-CHA is predominant in the process, and scission of the hexane ring and formation of short-chain carboxylic acids follows formation of these compounds. Additionally, concentration of heptadioidic acids in treated solution of CHA is very low contrary to treated solution of hydroxy-CHA (Figure 2). It suggests that reactions 23 and 24 may explain formation of short-chain carboxylic acids.

## 6. Conclusion

The mechanism of hydroxyl radical initiated degradation of a model OSPW alicyclic carboxylic acid revealed new information about the products and mechanisms of degradation. Contrary to predictions based on the reactivity of linear saturated aliphatic acids, hydroxyl radical attack did not take place preferentially at the  $\alpha$  tertiary carbon position; rather 4-oxo-CHA was the major byproduct in VUV and UV/H<sub>2</sub>O<sub>2</sub> systems, indicating that hydrogen atoms at the 4 position were the most vulnerable toward abstraction, possibly due to steric hindrance of the cyclohexane ring. Steric hindrance at the 4 position is also indicated by different reaction rate constants for *cis*- and *trans*-4-hydroxy-CHA; however, this further study with substituted CHA would confirm this hypothesis. By comparison of VUV and UV/H<sub>2</sub>O<sub>2</sub> processes, our results also suggest that H<sub>2</sub>O<sub>2</sub> can affect the reaction rate and yield of the byproduct. In UV/H<sub>2</sub>O<sub>2</sub>, direct reaction of H<sub>2</sub>O<sub>2</sub> with organic radicals and organic compounds slowed down the process.

## SCHEME 1: Proposed Mechanism of Hydroxyl Radical Induced Decomposition of CHA



Formation of oxo-, hydroxy-, and dioxo-CHA isomers was followed by formation of heptadioidic and short-chain carboxylic acids. It suggests that scission of the hexane ring induced by reaction with hydroxyl radical is characteristic only for the derivatives of CHA.

Degradation of CHA involves several reactions with hydroxyl radical. Thus, presence of other constituents reacting with



hydroxyl radicals, other than naphthenic acid, in treated water is important for efficiency of the process. Moreover, hydroxylated naphthenic acids may resemble sex steroids; thus the endocrine activity of UV/H<sub>2</sub>O<sub>2</sub> treated water should be considered. A proposed mechanism of the decomposition is depicted in Scheme 1.

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