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Photolytic dechlorination of 4-chlorophenol in O_2-saturated aqueous solutions in the absence of photocatalysts or additives using ArF* (193 nm) and KrF* (248 nm) excimer lasers

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Abstract

One of the toxic products from chlorine bleaching of wood pulp is 4-chlorophenol (4-CP). Detoxification of such compounds usually requires their dechlorination. The present study involves a fairly detailed comparison of the attempt and success of the photolytic dechlorination of 4-CP in O_2-saturated aqueous solutions using ArF* (193 nm) and KrF* (248 nm) excimer laser radiation at higher (1.1×10^{-2} M) and lower (4.5×10^{-4} M) starting substrate concentrations and comparisons of quantum yields (Φ), product distributions, etc.

At the higher starting substrate concentration (1.1×10^{-2} M) the average initial quantum yields, i.e. early in the reaction process, for the disappearance of 4-CP ($\Phi \approx 0.30$) and for the generation of chloride ions ($\Phi \approx 0.25$) were about the same for both 193 and 248 nm radiation. However, when the number of photons absorbed (n) became greater than about 3×10^{20}, more chloride ions (higher Φ) were generated with the 193 nm radiation than with the 248 nm radiation. Oligomers were the major products for both wavelengths of radiation, but the quantity of oligomers generated was greater using the 193 nm radiation. At 248 nm a significant amount of hydroquinone was generated, whereas hydroquinone was not detected with the 193 nm radiation. In addition, a significant amount of 4-chlorocatechol was generated during the direct photolysis of 4-CP using either wavelength of radiation. This is a new result for the photolysis of 4-CP at a wavelength longer than 193 nm in the absence of added H_2O_2.

At the lower starting substrate concentration (4.5×10^{-4} M) the average initial quantum yields for the disappearance of 4-CP ($\Phi \approx 0.55$) and for the generation of chloride ions ($\Phi \approx 0.45$) were both much greater using the 193 nm radiation than with the 248 nm radiation ($\Phi \approx 0.20$ and 0.10 respectively). At 193 nm oligomers were still the major products generated, but the fraction of oligomeric products generated was less than the fraction at the higher substrate concentration. This is consistent with the fact that at the lower substrate concentration a significant amount of hydroquinone was generated at 193 nm, whereas it was not detected at this wavelength for the higher substrate concentration. During the 248 nm photolysis of 4-CP at this lower starting substrate concentration, hydroquinone was the only major product generated in these experiments. Oligomers were not observed at this lower substrate concentration using 248 nm radiation, whereas oligomers were generated at the higher substrate concentration.

The results demonstrate the utility of using an excimer laser for the photolytic dechlorination of 4-CP without added photocatalysts or additives. It is also possible to suggest a number of explanations, given in the text, which are consistent with our findings.

Keywords: Direct photolysis; Photolytic dechlorination; Halogenophenols; Excimer lasers; Ultraviolet photolysis

1. Introduction

Chlorinated aromatic compounds are common pollutants in certain environments, which in part is a result of their generation and disposal by kraft mills in the bleaching of wood pulp [1]. These compounds are carcinogenic, mutagenic and some have a tendency to accumulate in fatty tissue. Therefore there is an interest in destroying or removing these compounds from the environment. One method for dechlorinating and thus reducing the toxicity of these compounds is by direct photolysis, particularly using radiation in the UV region of the spectrum.

In our study 4-chlorophenol (4-CP) was used as the model compound because a number of dechlorination studies have been done on it by others and in this laboratory, so that direct photolysis in aqueous solutions can be compared with them.

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Grabowski observed that with 313 nm radiation in aqueous alkali, chloro- and bromophenols underwent carbon–halogen bond cleavage with OH replacing the halogen atom [2]. Omura and Matsuura, using 253.7 nm radiation, found the major pathway for the dehalogenation of *p*-substituted halogenophenols in aqueous alkali to also be the homolytic cleavage of the carbon–halogen bond [3]. Crosby and Wong (300–450 nm) and Yasuhara et al. ($\lambda > 250$ nm) independently observed that 4-CP decomposed slowly with UV irradiation [4,5]. Boule et al. studied the direct photolysis (254 and 296 nm) of 4-CP in aqueous solution and determined the quantum yield to be about 0.40 for the disappearance of 4-CP. They found that this quantum yield was independent of (i) pH (1–13), (ii) substrate concentration (2×10^{-4}–1×10^{-2} M), (iii) wavelength of radiation (254 and 296 nm) and (iv) presence or absence of dissolved molecular oxygen. They also reported the quantum yield for the generation of chloride ions to be about 0.25, i.e. lower than for the disappearance of 4-CP [6–8]. Lipczynska-Kochany and Bolton developed a flash photolysis–high performance liquid chromatography (HPLC) method for studying photochemical reactions. Using broad spectrum Xe flash tubes as their light source, they also observed that the photoreaction of 4-CP was independent of pH and substrate concentration. In addition, unlike in other previous studies, dissolved molecular oxygen was found to be a participating reagent in the formation of the major initial product *p*-benzoquinone. The photoproduct 4-chlorocatechol was found when H_2O_2 was added to the solution [9–11]. Lipczynska-Kochany et al. detected five different radical species during the direct photolysis of 4-CP using electron spin resonance (ESR) spin-trapping detection, three of which were identified as radical intermediates: (i) H atom (or protonated hydrated electron), (ii) *p*-hydroxyphenyl radical ($R^{\cdot}$) and (iii) hydroxyl radical ($HO^{\cdot}$) [12]. Oudjehani and Bolton studied the direct 296 nm photolysis of 4-CP (2×10^{-3} and 2×10^{-4} M) in aerated aqueous solutions. The major product was found to be *p*-benzoquinone, with hydroquinone accounting for 30% of the initial formation of photoproducts at the lower starting substrate concentration. They detected 4-chlorocatechol as a very minor product but did not account for its generation [13]. Using a microsecond flash photometer (wavelengths not given), Durand et al. suggested in their flash-induced photolysis of 4-CP (5×10^{-4} M) that the initial step in this process is the formation of a radical cation. This intermediate radical cation, which was not detected, then undergoes secondary reactions to form *p*-benzoquinone. They also concluded that dissolved molecular oxygen does not play a direct role in the formation of *p*-benzoquinone, but it may prevent secondary reactions from occurring by some sort of quenching mechanism [14].

Jakob et al. used an Xe excimer emission lamp (172 nm) developed by Eliasson et al. [15] to study the oxidative degradation of aqueous solutions of 4-CP (5×10^{-4} M) in the vacuum UV (VUV) region of the spectrum. They found at this shorter wavelength that the dominant pathway for the oxidation of 4-CP was due to its reaction with hydroxyl radicals ($HO^{\cdot}$) derived from the photolysis of water. The quantum yield for the disappearance of 4-CP was determined to be 0.068 [16].

Recently Thomas et al. have demonstrated that 193 nm ArF* excimer laser radiation can effectively dechlorinate 4-CP in aqueous solutions. At their higher starting substrate concentration (1.07×10^{-2} M) the average initial quantum yields for the disappearance of 4-CP and for the generation of chloride ions were determined to be approximately 0.30 and 0.25 respectively. At their lower starting substrate concentration (4.49×10^{-4} M) the average initial quantum yields for the disappearance of 4-CP and for the generation of chloride ions were determined to be approximately 0.55 and 0.45 respectively. These initial quantum yields were observed to not be sensitive to the presence or absence of dissolved O_2 molecules. However, different products were favored at different substrate concentrations, which are attributable to the ensuing different substrate radical concentrations and somewhat to the presence or absence of solution O_2 [17–19].

There are very few data on the direct photolysis of 4-CP using deeper UV radiation in monochromatic form such as was employed in this study. This is one of the reasons for undertaking the present comparative study using ArF* (193 nm) and KrF* (248 nm) pulsed excimer lasers. It was hoped and found to lead to a greater understanding of the reactions involved during the photolytic dechlorination of 4-CP in O_2-saturated aqueous solutions.

2. Experimental details

The 193 nm radiation of an ArF* excimer laser (Lumonics Series TE-860-3) and the 248 nm radiation of a KrF* excimer laser (Lambda Physik LPX 300) were directed through the sample by using an appropriate 2-inch-diameter, 45° flat 95% reflector (Acton Research Corp.). Irradiations were carried out in a glass reactor which included a quartz window (Suprasil) 5 mm thick and a side-arm with a septum for sampling.

The direct photolysis of 4-CP by either the ArF* excimer laser or the KrF* excimer laser was carried out under O_2-saturated conditions. The reactor was filled with 350 ml of solution containing a starting substrate concentration of 1.1×10^{-2} or 4.5×10^{-4} M. Relatively small aliquots of sample (2–4 ml) were withdrawn every 5, 10, 15 or 20 min depending on the experiment for a total irradiation time of 2 h. The average power of the laser beam was also measured (Scientech 362 or Coherent Labmaster-E power meter) periodically during the experiments. Aliquot removals and power measurements were made to coincide very closely.

The concentrations of 4-CP, hydroquinone and 4-chlorocatechol were determined using HPLC and known concentration solutions of these compounds. HPLC separations were carried out with an Applied Biosystems HPLC apparatus

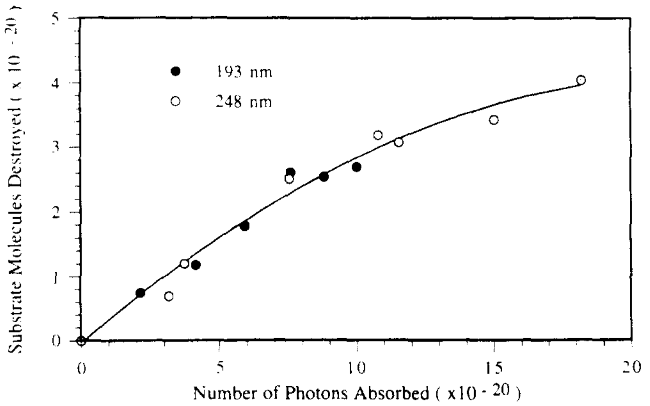

Fig. 1. Number of substrate molecules (4-CP) destroyed vs. number of photons absorbed during higher starting substrate concentration experiments (1.1×10^{-2} M).

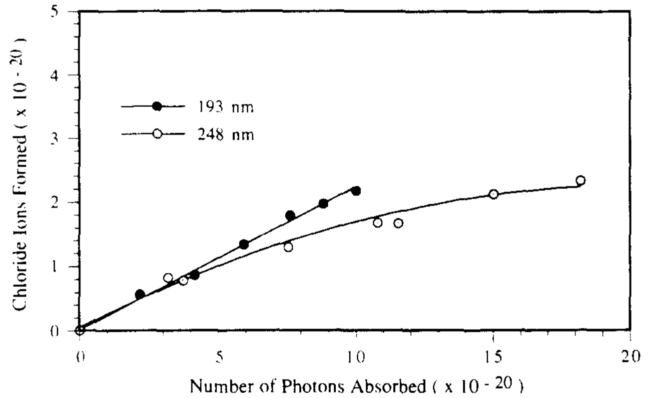

Fig. 2. Number of chloride ions generated vs. number of photons absorbed during higher starting substrate concentration experiments (1.1×10^{-2} M).

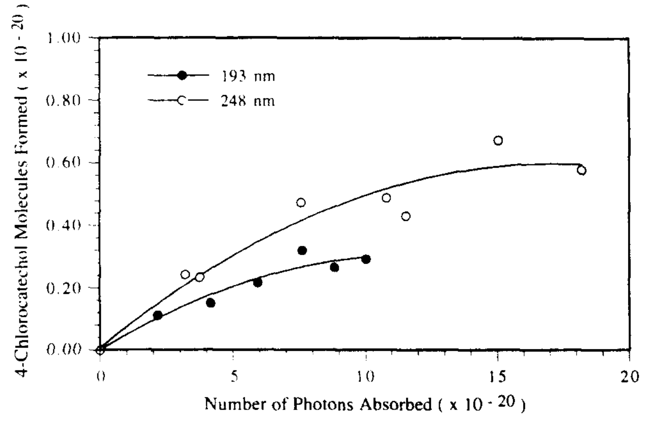

Fig. 3. Number of 4-chlorocatechol molecules generated vs. number of photons absorbed during higher starting substrate concentration experiments (1.1×10^{-2} M).

equipped with a Chromegabond C_{18} column; the absorbance detector was set to $\lambda=280$ nm and a Hewlett–Packard integrator–recorder was used. The solvent system consisted of HPLC grade acetonitrile, water and acetic acid (75:100:2 v/v/v).

The chloride ion concentration in solution was determined by ion exchange chromatography using solutions with known chloride ion concentrations. The experiments were carried out on a Dionex 2010i ion exchange chromatography instrument equipped with an AS 3 anion separator column. The eluant was 2.2 mM Na_2CO_3 + 0.75 mM $NaHCO_3$ in H_2O and the regenerant was 20–25 mN H_2SO_4; both were used at a flow rate of 2 ml min^{-1}.

3. Results

3.1. Solutions 1.1×10^{-2} M

As can be seen in Fig. 1, the rate of disappearance of 4-CP was very similar for both wavelengths of radiation (193 and 248 nm) at the higher starting substrate concentration (1.1×10^{-2} M). The average initial quantum yield for the disappearance of 4-CP was found to be approximately 0.30. The quantum yield for the disappearance of 4-CP was constant until about 5×10^{20} photons were absorbed. However, as the number of photons absorbed became large ($n>5\times10^{20}$), the quantum yield for the disappearance of 4-CP began to vary with n and became less than the initial value. This was probably the result of competition between the generated products and the substrate molecules (4-CP) for the photons entering the solution.

As can be seen in Fig. 2, the initial generation of chloride ions was about the same with both 193 and 248 nm radiation for this higher substrate concentration. Specifically, the average initial quantum yield for chloride ion generation was determined to be approximately 0.25 for both wavelengths. At 193 nm the quantum yield for the generation of chloride ions was constant at initial reaction conditions and continued to remain constant until about 10×10^{20} photons were absorbed (termination point of experiment). For the 248 nm radiation the quantum yield for the generation of chloride ions was also constant until about 3×10^{20} photons were absorbed, after which the quantum yield began to vary with n and its value became less than the initial value. This resulted in a lower chloride ion concentration build-up for the 248 nm radiation than for the 193 nm radiation for the same number of photons absorbed when $n>3\times10^{20}$.

Staying with the results for the solutions at the higher substrate concentration, the major products for both the 193 and 248 nm radiation were oligomers, which have been characterized in an earlier study [19]. However, 4-chlorocatechol was found to be generated to a significant extent by both wavelengths of radiation (Fig. 3). While it was reported that 4-chlorocatechol was generated as a major product in the 193 nm photolysis of 4-CP, there are no previous reports that 4-chlorocatechol was generated to any great extent using radiation with wavelengths longer than 193 nm in the absence of added H_2O_2 [19]. In fact, the concentration build-up of 4-chlorocatechol was greater for the 248 nm radiation than for the 193 nm radiation for all photon absorptions during the progress of the reaction.

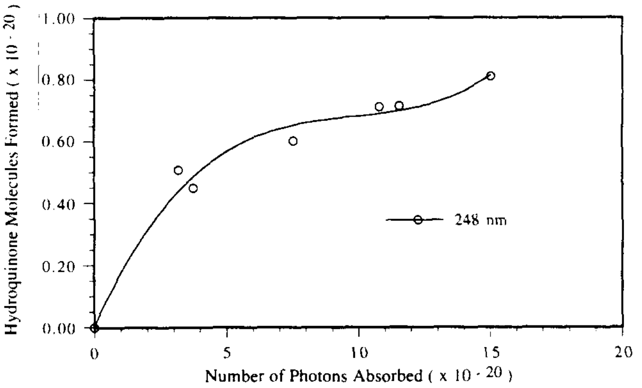

Fig. 4. Number of hydroquinone molecules generated vs. number of photons absorbed during higher starting substrate concentration experiments (1.1×10^{-2} M).

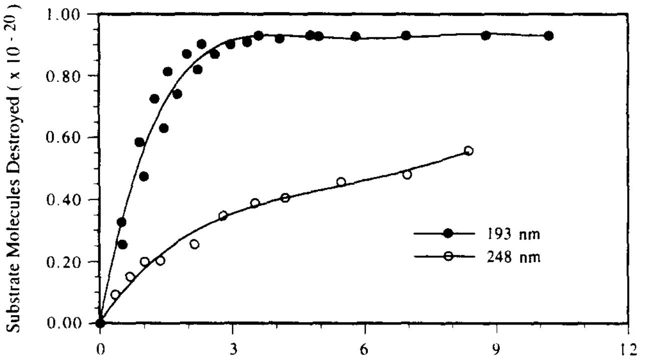

Fig. 5. Number of substrate molecules (4-CP) destroyed vs. number of photons absorbed during lower starting substrate concentration experiments (4.5×10^{-4} M).

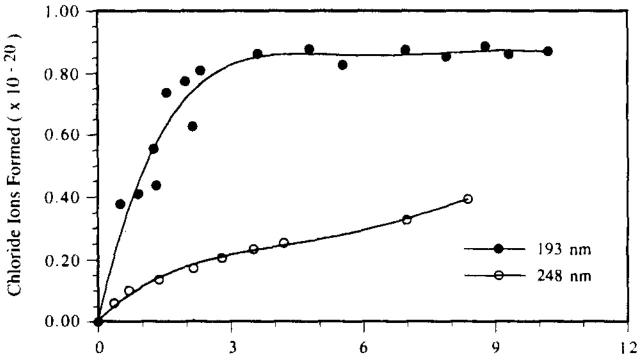

Fig. 6. Number of chloride ions generated vs. number of photons absorbed during lower starting substrate concentration experiments (4.5×10^{-4} M).

It was also found that hydroquinone was generated by the 248 nm radiation in these concentrated solutions (Fig. 4). On the other hand, at 193 nm the concentration of hydroquinone was too small to be detected at this higher substrate concentration. In fact, in these experiments with the 248 nm radiation the concentration build-up of hydroquinone was greater than the concentration build-up of 4-chlorocatechol for all photon absorptions during the progress of the reaction. Hydroquinone was also a major product detected by Boule et al. in their longer wavelength experiments (254 and 296 nm) in aerated aqueous solutions [6–8].

3.2. Solutions 4.5×10^{-4} M

As can be seen in Fig. 5, the average initial quantum yield for the disappearance of 4-CP was found to be much greater using 193 nm radiation ($\Phi \approx 0.55$) than using 248 nm radiation ($\Phi \approx 0.20$). Also, this initial quantum yield was constant for both 193 and 248 nm until about 1×10^{20} photons were absorbed. After a greater number of photons were absorbed ($n > 1 \times 10^{20}$), the quantum yields for the disappearance of 4-CP began to vary with n and became smaller than the initial value (owing to the competitive absorption of photons by generated products). By the time that about 4×10^{20} photons were absorbed, approximately 100% of the substrate molecules were destroyed by the 193 nm radiation, whereas only about 40% of the substrate molecules were destroyed by the 248 nm radiation.

With respect to chloride ion generation, Fig. 6 shows that the initial quantity of chloride ions produced per photon absorbed was linear for both wavelengths until about 1×10^{20} photons were absorbed. However, the average initial quantum yield for the generation of chloride ions was much greater for the 193 nm radiation ($\Phi \approx 0.45$) than for the 248 nm radiation ($\Phi \approx 0.10$). After about 4×10^{20} photons were absorbed by each of the two identical solutions, approximately 90% of the total possible amount of chloride ions was generated by the 193 nm radiation, whereas only about 25% of the possible amount of chloride ions was generated by the 248 nm radiation.

It is also of interest that for this lower substrate concentration, different major products were generated by the 193 and 248 nm photons. Oligomers were still a major product generated by the 193 nm radiation as they were at the higher substrate concentration. However, a significant amount of hydroquinone was also generated as another major product in these experiments. Oligomers were not generated by the 248 nm radiation at this lower substrate concentration. In these experiments using 248 nm radiation, hydroquinone was the only major product generated.

Finally, for both substrate concentrations the average initial quantum yields for the disappearance of 4-CP were larger than the average initial quantum yields for the generation of chloride ions for each wavelength of radiation used in these experiments. In what follows, these results described above are reconciled with the reagents used (4-CP, O_2 and H_2O) and their chemical behavioral differences toward 193 and 248 nm photons.

4. Discussion

The several results described above are consistent with the following explanations. At the outset we were able to conclude that the photolytic dechlorination of 4-CP with chloride ion formation was attributable to a dominantly free-radical formation mechanism ($R^{\bullet}$ and $Cl^{\bullet}$) rather than the other likely alternative, that of oxidative degradation by the action of hydroxyl radicals (high redox potential, $E^{\circ} = 2.80$ V) with $HO^{\bullet}$ derived from the photolysis of water. This conclusion is based on the following. First, for the 193 nm radiation we compared the number of photons absorbed by water ($\epsilon_{192.5} = 1.28 \times 10^{-3}$ M^{-1} cm^{-1} [20]) and 4-CP ($\epsilon_{193} \approx 4.4 \times 10^4$ M^{-1} cm^{-1}, present experiment). Since the number of photons absorbed is directly related to the number of molecules in solution, the ratio of the number of photons absorbed (n) by R–Cl and H_2O can be calculated by using Eq. (1) shown below.

$$\frac{n(\text{Rl–Cl abs})}{n(\text{H}_2\text{O abs})} = \frac{\epsilon_{\text{R–Cl}} M_{\text{R–Cl}}}{\epsilon_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}} \tag{1}$$

In the present work $M_{\text{R–Cl}}$ (the lower starting substrate concentration) was approximately 4.5×10^{-4} M and M_{H_2O} was approximately 55.35 M at 25 °C. Thus the ratio of the number of photons absorbed was approximately 280:1 (R–Cl:H_2O) for the 193 nm radiation. Therefore approximately 280 photons were absorbed by the substrate molecules for every molecule of H_2O that absorbed a photon. Then, assuming quantum yields were 1.0 for reactions (2) and (3) shown below, the number of $R^{\bullet}$ radicals generated was about 280 times that of $HO^{\bullet}$ radicals generated. Therefore, the homolytic cleavage of the C–Cl bond in reaction (3) was considered to be the dominant pathway for substrate dechlorination when 193 nm radiation was used at both starting substrate concentrations.

$$H_2O(l) \longrightarrow \tfrac{1}{2}H_2(g) + HO^{\bullet}(aq) \tag{2}$$

$$R\text{–}Cl \longrightarrow R^{\bullet} + Cl^{\bullet} \tag{3}$$

Switching our attention to the experiments using 248 nm radiation, now H_2O is not a source for $HO^{\bullet}$ radicals (no electronic absorption by H_2O), so the formation of $R^{\bullet}$ via homolysis (3) was the only direct pathway to oxidative degradation. This substrate free-radical mechanism has also been substantiated by the detection of $R^{\bullet}$ (*p*-hydroxyphenyl radical) during the direct photolysis of aerated aqueous solutions of 4-CP using broad spectrum Xe flash tubes as the light source [12]. The subsequent fates of this organic radical ($R^{\bullet}$) can in principle be several. Some of the possible reactions which $R^{\bullet}$ may undergo are shown below and, as will be discussed, are consistent with our observations [21].

$$R^{\bullet} + Cl^{\bullet} \longrightarrow R\text{–}Cl \quad \text{(recombination)} \tag{4}$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R_2 \quad \text{(oligomerization)} \tag{5}$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \quad \text{(peroxyl radical formation)} \tag{6}$$

When the higher concentration solution of 4-CP (1.1×10^{-2} M) was irradiated, we found that the 193 nm radiation produced a larger fraction of oligomers than that produced by the 248 nm radiation. To account for this result, comparisons need to be made of what happens per pulse of radiation. In the subsequent steps, where one needs to know the solution reaction volume per laser pulse (V_{λ}), we are interested in the radiation penetration length (l_{λ}) when the beam intensity of the light within the solution has been diminished to 1% of its original intensity. At the higher starting substrate concentration the radiation penetration lengths were calculated to be $l_{193} \approx 4.1 \times 10^{-3}$ cm ($\epsilon_{193} \approx 4.4 \times 10^4$ M^{-1} cm^{-1}) and $l_{248} \approx 0.43$ cm ($\epsilon_{248} \approx 420$ M^{-1} cm^{-1}, present experiment). The illumination areas were approximately 1.2 cm^2 (193 nm) and 2.8 cm^2 (248 nm). From these dimensions the solution reaction volumes per laser pulse were calculated to be $V_{193} \approx 4.9 \times 10^{-3}$ cm^3 and $V_{248} \approx 1.2$ cm^3. Based on these reaction volumes, we then calculated the generated substrate radical concentration per laser pulse by using the average measured laser energies ($E_{193} \approx 0.024$ J per pulse and $E_{248} \approx 0.19$ J per pulse), assuming the quantum yield for homolysis (3) was 1.0 for both wavelengths. At the higher starting 4-CP concentration the calculated substrate radical concentrations per laser pulse were approximately 7.9×10^{-3} M (193 nm) and 3.3×10^{-4} M (248 nm). One would expect that the greater amount of oligomeric material would be generated in the more concentrated solution of substrate radicals, because reaction (5) becomes more favorable. In fact, this was found to be the case, i.e. the mass of collected oligomeric material was 4.33 mg following 193 nm irradiation compared with 2.00 mg following 248 nm irradiation. When the number of photons absorbed for each wavelength was calculated, it was experimentally found that per photon absorbed there was in fact about 3.5 times more oligomeric material generated by the 193 nm radiation than by the 248 nm radiation. This is consistent with the homolytic cleavage of the C–Cl bond in reaction (3) being the dominant pathway for the dechlorination of 4-CP.

Next, it is also of relevance to compare the generated substrate radical concentration [$R^{\bullet}$] discussed in the foregoing paragraph with the concentration of dissolved O_2 molecules (1.29×10^{-3} M at 25 °C in H_2O [22]) in the orthorhombically shaped reaction volume as defined by each laser pulse. There were approximately six times as many substrate radicals ($R^{\bullet}$) as O_2 molecules in the reaction volume of the 193 nm pulse, whereas one has almost the reverse situation with approximately four times as many O_2 molecules as $R^{\bullet}$ radicals in the reaction volume of the 248 nm pulse. Therefore the $R^{\bullet}$ radicals generated by the latter 248 nm radiation were more likely to be trapped by the dissolved O_2 molecules (6), generating peroxyl radicals ($RO_2^{\bullet}$), than were substrate radicals generated by the 193 nm radiation. This anticipation was substantiated experimentally by finding generated hydroquinone using 248 nm radiation but not with the 193 nm radiation. In other words, the presence of hydroquinone suggests the formation of the precursor intermediate $RO_2^{\bullet}$, i.e. hydroquinone formation can be a result of the decomposition of $RO_2^{\bullet}$ in aqueous solutions [19] (see text of Appendix and Eqs. (A1)–(A5)).

Now we turn our discussion to the results obtained with the lower starting substrate concentration (4.5×10^{-4} M).

Again we estimated the generated substrate radical concentration per laser pulse as was done for the higher substrate concentration. The solution reaction volumes were $V_{193} \approx 0.12$ cm^3 and $V_{248} \approx 31$ cm^3 ($l_{193} \approx 0.10$ cm and $l_{248} \approx 11$ cm). In these experiments the average measured energies were $E_{193} \approx 0.021$ J per pulse and $E_{248} \approx 0.093$ J per pulse. Therefore the calculated substrate radical concentrations were approximately 2.8×10^{-4} M (193 nm) and 6.2×10^{-6} M (248 nm). Consequently, the estimated substrate radical concentration was about 45 times greater for the 193 nm radiation than for the 248 nm radiation. Therefore we expected and found oligomerization to be much greater using the 193 nm radiation (oligomers were still a major product) than using the 248 nm radiation (no oligomers were observed) for this lower starting substrate concentration.

As was done for the higher substrate concentration described above, we compared the concentration of generated $R^\bullet$ radicals per laser pulse with the concentration of dissolved O_2 molecules (1.29×10^{-3} M). For a 193 nm pulse the concentration of dissolved O_2 molecules was about 4.6 times larger than the concentration of $R^\bullet$ radicals, whereas for a 248 nm pulse the concentration of dissolved O_2 molecules was about 210 times greater than the concentration of $R^\bullet$ radicals. Therefore, reasoning that if this $[O_2]:[R^\bullet]$ ratio factor was important, we would expect to find that hydroquinone and oligomers would both be major products when using the 193 nm radiation. This was what we indeed found to be the case experimentally. Also consistent with this suggested $[O_2]:[R^\bullet]$ ratio factor is that hydroquinone was the only major product generated using the 248 nm radiation at this lower substrate concentration (no oligomers were observed). The reason this was expected and found to be true experimentally was that the generated $R^\bullet$ concentration (6.2×10^{-6} M) per 248 nm pulse was so small that oligomerization (5) became negligible. Therefore the only reaction pathway for the disappearance of 4-CP was reaction (6). The decomposition of $RO_2^\bullet$ leads to the formation of hydroquinone, which was the only major product observed at 248 nm for this lower starting substrate concentration [19] (see text of Appendix and Eqs. (A1)–(A5)).

It is also of interest to note the photolytic formation of 4-chlorocatechol as a major product from 4-CP during 248 nm photolysis at the higher substrate concentration. We have reported 4-chlorocatechol to be a major product in the shorter wavelength 193 nm photolysis of 4-CP in the absence of any added H_2O_2 [19]. However, its generation has also been reported during the photolysis of 4-CP at longer wavelengths only in the presence of added H_2O_2 (source of hydroxyl radicals) [11]. In the literature the generation of 4-chlorocatechol in aqueous solution is suggested to be the result of $HO^\bullet$ radicals (from radiolysis [23]) reacting with substrate molecules (see text of Appendix and Eq. (A9)). In our experiments these $HO^\bullet$ radicals were probably generated primarily as a byproduct (i) during the formation of hydroquinone from the decomposition of $RO_2^\bullet$ [19] (see text of Appendix and Eqs. (A1)–(A5)) and (ii) accompanying the reduction of chlorine radicals (generated from the homolysis of the substrate) to chloride ions by the reaction shown below [24] (see text of Appendix and Eqs. (A6)–(A8)).

$$Cl^\bullet + H_2O \longrightarrow HO^\bullet + Cl^- + H^+ \qquad (7)$$

As discussed above, the formation of $HO^\bullet$ radicals from the direct photolysis of $H_2O(l)$ at 193 nm is negligible and it does not occur at 248 nm because $H_2O(l)$ is transparent at this wavelength. Being related to 4-chlorocatechol formation, we also address the observation that at this higher substrate concentration the quantum yield (Φ) for 4-chlorocatechol generation was greater at 248 nm than at 193 nm (Fig. 3). In turn, this greater Φ for 4-chlorocatechol generation at 248 nm also suggests surprisingly that at 248 nm a greater amount of $HO^\bullet$ was generated than at 193 nm, because 4-chlorocatechol can result from $HO^\bullet$ radicals reacting with 4-CP [23] (see text of Appendix and Eq. (A9)). It is also important to note that $HO^\bullet$ radicals have been detected in the photolysis of 4-CP in aqueous solutions in the absence of added H_2O_2 [12]. In order to explain our observations described above of the greater amount of 4-chlorocatechol generation at 248 nm, we will now discuss the two possible sources for these $HO^\bullet$ radicals. First of all, as was mentioned above, we found that Φ for Cl^- generation was greater at 193 nm than at 248 nm (Fig. 2). Therefore the quantity of $HO^\bullet$ radicals generated as a byproduct from reaction (7) would also be greater at 193 nm than at 248 nm. However, the greater Φ for 4-chlorocatechol generation at 248 nm suggests that more $HO^\bullet$ radicals were generated during the 248 nm photolysis than during the 193 nm photolysis. This may be attributed to the fact that hydroquinone was generated at 248 nm but not at 193 nm. In the formation of hydroquinone, $HO^\bullet$ radicals are also generated as a byproduct in the decomposition of $RO_2^\bullet$ [19] (see text of Appendix and Eqs. (A1)–(A5)). Therefore, at least two possible sources for $HO^\bullet$ radicals were operative at 248 nm (larger Φ for 4-chlorocatechol generation) compared with only one source at 193 nm. These observations were also consistent with finding the smaller Φ for Cl^- generation at 248 nm rather than at 193 nm for large photon absorptions ($n > 3 \times 10^{20}$), i.e. more chlorine remained in the photoproducts (4-chlorocatechol, oligomers, etc.).

With the 193 nm radiation the average initial quantum yields for the disappearance of 4-CP and for the generation of Cl^- increased when the starting substrate concentration was decreased. We attribute this to recombination (4) being less favored for the lower starting substrate concentration than for the higher starting substrate concentration, thus increasing the initial quantum yields. We expected that oligomerization (5) would be less favored for the lower substrate concentration than for the higher substrate concentration, which would lower the initial quantum yields. This was indeed found to be the case. However, the decrease in the quantity of oligomers generated appears to have been more than offset by the generation of hydroquinone at the lower substrate concentration, which was not generated by the 193 nm radiation at the higher substrate concentration. Therefore the disappearance of 4-CP and the generation of Cl^- involved both reactions (5) and (6) for the lower substrate concentration, whereas for the higher substrate concentration only reaction (5) was involved. All these factors described above may account for the larger average initial quantum yields for the disappearance of 4-CP and for the generation of Cl^- at the lower substrate concentration than at the higher substrate concentration using 193 nm radiation.

When the substrate concentration was decreased (from 1.1×10^{-2} to 4.5×10^{-4} M), the average initial quantum yields at 248 nm for the disappearance of 4-CP and for the generation of Cl^- decreased. At the higher substrate concentration both oligomerization (5) and the generation of peroxyl radicals (6) were the major reaction results for the disappearance of 4-CP. At the lower substrate concentration the generated substrate radical concentration per laser pulse was estimated to be so small (6.2×10^{-6} M) compared with $[R^\cdot]$ at 193 nm (7.9×10^{-3} M) that oligomerization was not expected to take place. Indeed, it was not found to be an important reaction. Therefore at the lower substrate concentration only reaction (6) was important for the disappearance of 4-CP and the generation of Cl^-. On the other hand, at least two reactions ((5) and (6)) are operative at the higher starting substrate concentration. This conclusion is again consistent with finding smaller initial quantum yields for (i) the disappearance of 4-CP and (ii) the generation of Cl^- at the lower substrate concentration using 248 nm radiation.

Finally, it was observed for both wavelengths of radiation and for both starting substrate concentrations that the average initial quantum yields for the disappearance of 4-CP were always larger than the average initial quantum yields for the generation of Cl^-. This can be understood to be the result that each event of substrate disappearance does not immediately lead to an event of Cl^- generation, i.e. some of the chlorine of the substrate ended up in other photoproducts (4-chlorocatechol, oligomers, etc.).

The present research was undertaken to determine the feasibility of dechlorinating aromatic compounds found in kraft mill effluents using UV excimer lasers without added photocatalysts, H_2O_2, etc. In another approach a number of studies on the degradation of 4-CP by heterogeneous photocatalysis have been carried out [25–38]. In addition, other advanced oxidative processes such as UV/H_2O_2 [39–42], UV/O_3 [43–46], etc. have also been used in the degradation of similar compounds in aqueous solutions.

5. Conclusions

The utility of using UV radiation produced by excimer lasers for the photolytic dechlorination of 4-CP has been demonstrated and compared for the ArF* (193 nm) and KrF* (248 nm) excimer lasers. At the lower starting substrate concentration (4.5×10^{-4} M) it was found that the average quantum yields for the initial disappearance of 4-CP ($\Phi \approx 0.55$) and for the initial generation of Cl^- ($\Phi \approx 0.45$) were greater for the 193 nm radiation than for the 248 nm radiation, i.e. $\Phi \approx 0.20$ (disappearance of 4-CP) and $\Phi \approx 0.10$ (generation of Cl^-). However, at the higher starting substrate concentration (1.1×10^{-2} M) the average quantum yields for the disappearance of 4-CP ($\Phi \approx 0.30$) and for the generation of Cl^- ($\Phi \approx 0.25$) were approximately the same for both wavelengths. Also, it is important to note the generation of 4-chlorocatechol as a major product during 193 and 248 nm irradiations at the higher substrate concentration. This is the first time that 4-chlorocatechol has been reported as a major product from the direct photolysis of 4-CP using a wavelength of radiation longer than 193 nm and in the absence of added H_2O_2.

There is a significant wavelength influence on the distribution of photolysis products. This can be understood to be a consequence of the concentration of generated substrate radicals compared with the concentration of dissolved O_2 molecules in the solution reaction volume of the laser pulse. At the higher starting substrate concentration and using 193 nm radiation, the concentration of generated substrate radicals was larger than the concentration of dissolved O_2 molecules in the solution reaction volume (7.9×10^{-3} M vs. 1.29×10^{-3} M). The major product generated was oligomeric material (hydroquinone was not detected). However, for the lower starting substrate concentration and using 193 nm radiation, the concentration of dissolved O_2 molecules was larger than the concentration of generated substrate radicals in the solution reaction volume (1.29×10^{-3} M vs. 2.8×10^{-4} M). In this case the major products generated were oligomers and hydroquinone. These same two products were also found to be the major products generated during 248 nm irradiation at the higher starting substrate concentration. In these experiments the concentration of dissolved O_2 molecules was also larger than the concentration of generated substrate radicals in the solution reaction volume (1.29×10^{-3} M vs. 3.3×10^{-4} M). Finally, at the lower starting substrate concentration and using 248 nm radiation, the concentration of dissolved O_2 molecules was much greater than the concentration of generated substrate radicals (1.29×10^{-3} M vs. 6.2×10^{-6} M). Under these conditions the only major product generated was hydroquinone (oligomers were not observed).

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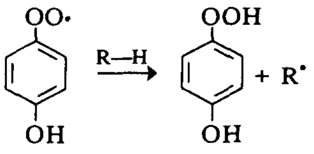
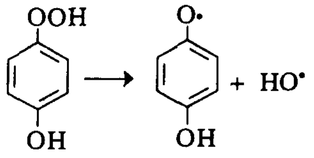
Appendix

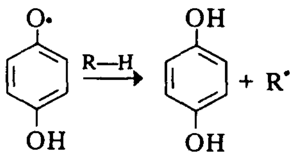
From previous work, whose references are given, several possible reactions may account for our findings for the formation of (i) hydroquinone, (ii) Cl^- and (iii) 4-chlorocatechol and are given below. First, the formation of hydroquinone from the unstable peroxyl radical ($RO_2^{\bullet}$) generated in reaction (6) shown above may involve at least two possible pathways. The first of these may be the result of reactions (A1)–(A3) shown below. A second conceivable pathway that may occur in a highly concentrated pocket of peroxyl radicals may consist of reactions (A4), (A5) and (A3) in that order also shown below [19,47].



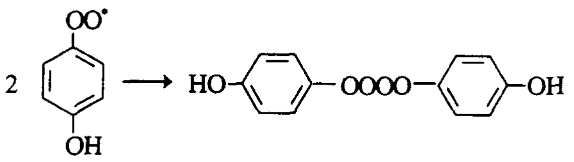
(A1)



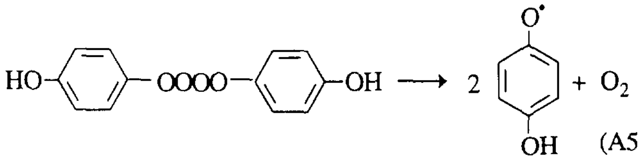
(A2)



(A3)



(A4)


(A5)

It is important to note that the first of these proposed pathways generates $HO^{\bullet}$ radicals. The presence of $HO^{\bullet}$ radicals may be important in the generation of 4-chlorocatechol, which was a major product generated during both the 193 and 248 nm irradiations at the higher starting substrate concentration [23].

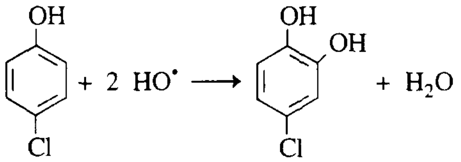
The chlorine radicals ($Cl^{\bullet}$) generated in reaction (3), derived from the direct photolysis of 4-CP, can possibly react with water molecules, considering the large molarity of $H_2O(l)$. According to McElroy, reactions (A6)–(A8) shown below may account for the reduction of $Cl^{\bullet}$ to Cl^- and may also be a source for $HO^{\bullet}$ radicals [24]. The sum of reactions (A6)–(A8) results in reaction (7), which was given above.

$$H_2O + Cl \longrightarrow HOClH \qquad (A6)$$

$$HOClH \longrightarrow HOCl^- + H^+ \qquad (A7)$$

$$HOCl^- \longrightarrow HO + Cl^- \qquad (A8)$$

Finally, the formation of 4-chlorocatechol is likely the result of 4-CP reacting with $HO^{\bullet}$ radicals. Both the generation of hydroquinone and that of Cl^- discussed above may be sources for these $HO^{\bullet}$ radicals. Also, the presence of $HO^{\bullet}$ radicals in the direct photolysis of 4-CP in aqueous solutions has been determined experimentally [12]. There may be at least two possible pathways for the generation of 4-chlorocatechol from the reaction of $HO^{\bullet}$ radicals with 4-CP. First, an $HO^{\bullet}$ radical may react with 4-CP to form the intermediate hydroxycyclohexadienyl radical, which upon disproportionation generates 4-chlorocatechol and water [23]. The generation of 4-chlorocatechol may also involve this same radical intermediate, but instead of disproportionating, another $HO^{\bullet}$ (or $R^{\bullet}$) abstracts a hydrogen atom from this radical intermediate. This again would result in the formation of 4-chlorocatechol and water. The overall reaction for both these possible pathways is reaction (A9) shown below [19].


(A9)