Photocatalytic Degradation of 4-Chlorophenol. 2. The 4-Chlorocatechol Pathway

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The TiO_2-mediated photocatalytic degradation of 4-chlorocatechol is studied as a branch of the degradation of 4-chlorophenol. In addition to some basic kinetic studies, the identities of many of the cyclic and acyclic intermediates, verified in most cases with authentic samples, are reported. From 4-chlorocatechol, the major product is hydroxylation to form 5-chloro-1,2,4-benzenetriol. A small amount of 4-chloropyrogallol is also produced. Substitution to give 1,2,4-benzenetriol is observed as is oxidative cleavage of the C1−C2 bond to give the diacid. The major products of all of the triols are those of oxidative cleavages, occurring mainly between *ortho* hydroxy-substituted carbons to give diacids but also between one hydroxy and one unsubstituted carbon to give acid-aldehydes. Many smaller intermediates in the degradations are identified, and pathways are proposed for the larger compounds.

Introduction

The photocatalytic degradation of 4-chlorophenol by TiO_2 and other semiconductor catalysts has taken on an importance in the literature that exceeds its original significance as a model pollutant.[1] It has become a standard for evaluating experimental parameters and examining their effects on mechanism and efficiency.[2−36] Many of these publications focus on practical aspects of photocatalysis as an advanced oxidation process for cleanup of contaminated waters. Others are concerned with the effect of experimental parameters on either the initial disappearance of the 4-chlorophenol or the total mineralization rate.

A third category of papers is concerned with the chemical mechanisms of the degradation and the pathways by which chlorophenol is degraded to CO_2 and Cl^-. The oxidative mineralization chemistry can involve a number of reactive species, such as TiO_2-bound hydroxyl radicals, TiO_2 valence band holes, superoxide, and other less reactive oxidizers such as molecular oxygen and hydrogen peroxide.

It is well established that, using TiO_2 as the photocatalyst, two reactions compete as the first transformation, giving hydroquinone and 4-chlorocatechol (Scheme 1).[2,3,21,37,38] Differences in the observed ratios of these two reactions have been reviewed by Stafford.[29,33] Despite the plethora of information available about the first chemical step, little is known about the subsequent chemistry that leads to ring opening and further degradation of acyclic compounds. For instance, the first carbon−carbon cleav-

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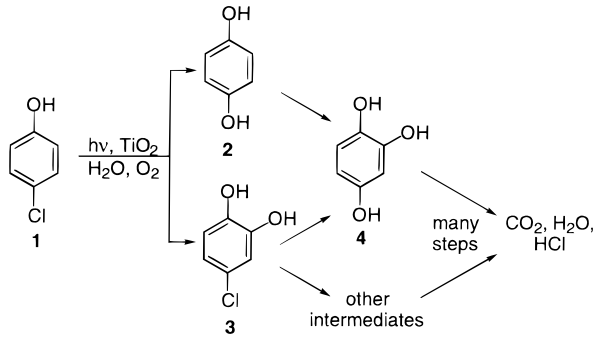
Scheme 1

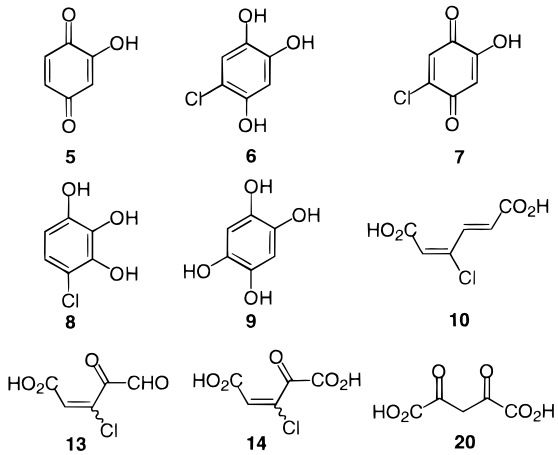


age step is of obvious fundamental interest, reflecting the nature of the oxidative step. We have examined the degradation of 4-chlorophenol by TiO_2 using HPLC and GC−MS analysis of the intermediates in combination with organic synthesis of the proposed intermediates to take a more detailed look at this chemistry. In the first paper of this series,[39] we reported over 20 intermediates observed in the degradation of hydroquinone, representing that branch of the degradation of chlorophenol. Here we report a similar study of the degradation of 4-chlorocatechol, the other major product of the first step of 4-chlorophenol photocatalytic degradation. Together, these give a complete set of data for the degradation intermediates of 4-chlorophenol under TiO_2-mediated photocatalytic degradation and provide insight particularly into the ring-opening reaction for simple aromatic compounds. We also characterize the degradation of 4-chlorocatechol as a function of pH and catalyst load.

Results

Photocatalytic Degradation of 4-Chlorophenol. A set of standard conditions was established for degradation of 4-chlorophenol **1** and other compounds. Solutions of 100 mL buffered water (5 mM phosphate, pH 7.0 unless otherwise specified) containing 2 mM of substrate were prepared, and 50 mg Degussa P-25 TiO_2 was added. The solutions were treated in an ultrasound bath and then saturated with O_2 before photolysis. The concentrations of starting materials and various intermediates were determined by HPLC analysis with a UV−vis diode array detector. The concentration of miscellaneous degradation products were determined or approximated as described in the Experimental Section.

For degradation of **1**, intermediates were detected by HPLC with retention times of 1.2, 1.7, 2.7, 3.6, 6.6, 12.1, and 15.0 min. As was found previously,[39] the 1.2 min peak consisted of a number of ring-opened intermediates. The 1.7 min peak was a mixture of compounds. On the basis of their new appearance compared to degradations of **4**, they were tentatively assigned as chlorine-containing structures. The peaks at 3.6, 6.6, 12.1, and 15.0 min were assigned to **2**, **5**, **7**, **3**, and **1**. 1,2,4-Benzentrol is very easily oxidized to **5**,[40] and it was established that this also occurs during the HPLC analysis procedure. Compound **6** is also easily oxidized to **7**. 4-Chlororesorcinol, 2,5,4′-trihydroxybiphenyl, phenol, and 4′-hydroxyphenylbenzoquinone, which have been reported by others,[21,38] were not observed. On the time scale of these experiments, intermediates formed in dark control reactions were insignificant.



The variation of the concentrations of major intermediates as a function of time is illustrated in Figure 1. The solution was completely mineralized in about 800 min. Among the cyclic intermediates, the halogen-containing compounds predominate over the others under our standard conditions. The ratio of maximum concentration of intermediates **3** and **2** is 2.8. This compares favorably to the results of Mills[21] and Stafford.[29] The values of $[\text{intermediates}]_{max}/[\mathbf{1}]_0$ are 0.036, 0.017, 0.072, and 0.10 for **2**, **5**, **7**, and **3**, respectively, after 80 min irradiation (near the maximum concentration for these compounds), also similar to Mills' results, save that they do not report **6** or **7**. The rate constants of photodegradation of **1**−**3**, independently measured and given in Table 1, are similar. Thus, the reason more **3** is observed in degradations of **1** is its slight predominance in formation and not selective degradation of **2**.

A series of degradations was carried out using the standard conditions but adding 1% (by volume) 2-propanol. The rate of photocatalytic decay of all compounds was substantially lower in these experiments, but that of hydroquinone dropped to the extent that it was no longer competitive with other dark processes (Table 1). Figure 2 illustrates the early development of intermediates in the degradation of **1** with 2-propanol present. The intermediates that have the 1,2-oxygen functionality are selectively destroyed over hydroquinone, as would be predicted from Table 1.

Photocatalytic Degradation of 4-Chlorocatechol. Degradations were carried out using **3** as starting material in standard conditions. Control experiments neglecting one of the three components (O_2, TiO_2, and light) were performed. In the absence of oxygen, no change in the concentration of **3** was observed over 21 h despite exposure to light in the presence of TiO_2. Direct photolysis can thus be neglected. Dark experiments that included O_2 and TiO_2 showed a slow autoxidation at pH 7.0. Less than 7% of **3** was degraded after 10 h. A rough estimate of 1×10^{-4} min^{-1} could be made for the pseudo-first-order rate constant. With light and oxygen but no TiO_2, 20% of **3** was degraded after 10 h. However, none of the cyclic intermediates discussed below were among the products. Such oxygenative cleavage of chlorocatechols has been reported elsewhere[41] but did not appear to be significant,

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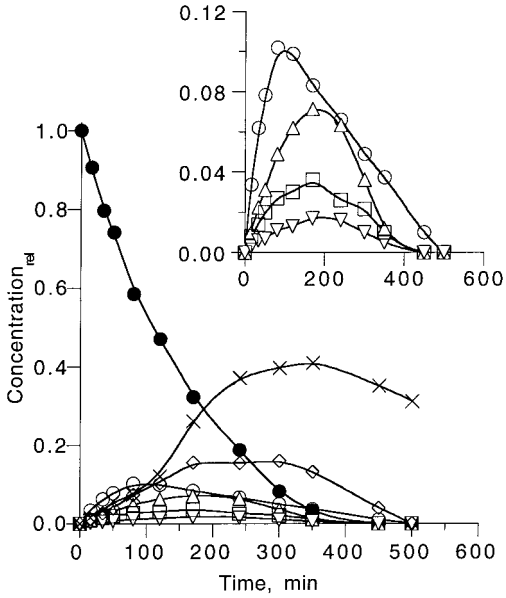

Figure 1. Photocatalytic decay of an oxygen-saturated aqueous solution of 4-chlorophenol (filled circles) and formation of intermediates 4-chlorocatechol (circles), 5-chloro-2-hydroxybenzoquinone (triangles), hydroxybenzoquinone (inverted triangles), hydroquinone (squares), unidentified chlorinated mixture (diamonds), and acyclic acids (×). The inset is a blow up of the early time period.

Table 1. Pseudo-First-Order Rate Constants for Decay of 1, 2, 3, and 7 under Standard Conditions

		rate constant (10^{-3} min^{-1})		
compd	pH	photocatalytic decay	photocatalytic decay with 1% ^{i}PrOH	dark decay
1	7.0	6.9	1.0	0.11
2	7.0	6.8	0.48	0.49
3	7.0	6.6	2.1	0.11
7	7.0	13	3.3	1.5
3	2.0	3.7[a]		
3	4.0	4.2[a]		
3	8.5	15[a]		

[a] Rate constant corrected by subtraction of the dark decay rate constant from the total decay rate constant with the light on.

because with the full standard conditions, the decay was much more rapid. 4-Chlorocatechol was completely decomposed in 450 min.

Using HPLC detection, degradation of **3** gave rise to five peaks with retention times of 1.2, 1.3, 1.6, 3.6, and 6.7 min. As usual, the first peak was a combination of acyclic acids. The peaks at 3.6 and 6.7 min were identified as **5** and **7**, representing the total concentrations of (**4** and **5**) and (**6** and **7**), respectively. The other two peaks represented mixtures of compounds and were not further identified by HPLC (Figure 3).

The effect of pH on the degradation of **3** was investigated. The pseudo-first-order rate constants, corrected by subtraction of the appropriate dark decay rate constants, are given in Table 1. Whereas there is some decrease in the rate as the solution becomes acidic, a dramatic increase is noted when the pH is raised to 8.5. The trials could not be extended above this pH because of base-catalyzed dark decomposition of **3** in the presence of oxygen. At pH 10, **3** completely decomposed in 10 min, even in the absence of light. The number and identity of detectable intermediates was relatively constant throughout the pH range discussed here, but their concentrations were highest at neutral pH, so this was chosen for the experiments below in which the identities of the intermediates were determined.

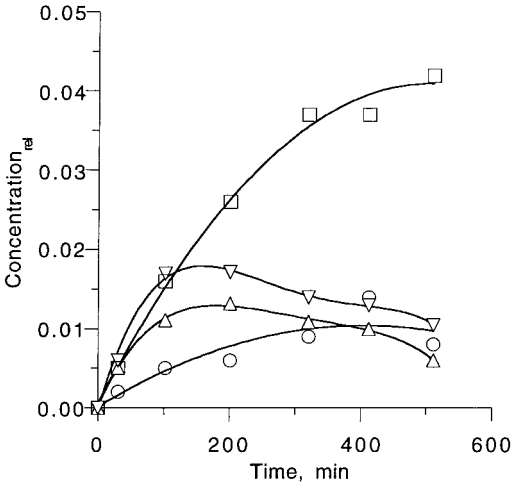

Figure 2. Kinetics of the photocatalytic decay of an oxygen-saturated aqueous solution of 4-chlorophenol with 1% 2-propanol added. Shown is formation of 4-chlorocatechol (circles), 5-chloro-2-hydroxybenzoquinone (triangles), hydroxybenzoquinone (inverted triangles), and hydroquinone (squares).

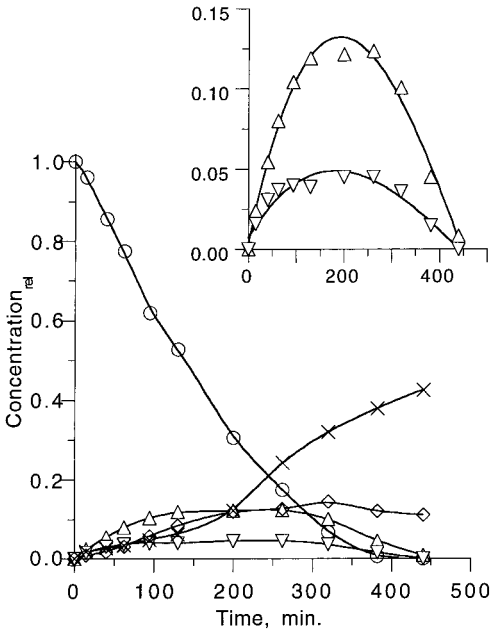

Figure 3. Photocatalytic decay of an oxygen-saturated aqueous solution of 4-chlorocatechol (circles) and formation of intermediates 5-chloro-2-hydroxybenzoquinone (triangles), hydroxybenzoquinone (inverted triangles), unidentified intermediate (diamonds), and acids (×). The inset shows only 5-chloro-2-hydroxybenzoquinone and hydroxybenzoquinone.

As expected for photocatalytic reactions, degradations that were done without buffer resulted in acidification of the solution. An unbuffered solution of **3** whose initial pH was adjusted to 7.0 with NaOH was at pH 4 with only 5% of the compound degraded (Figure 4). This is, of course, a result of the dramatic effect on pH of a small amount of acid production in the higher pH ranges. The final pH was 2.76, matching well with the final theoretical value of 2.70, neglecting buffering by TiO_2 or carbonic acid.

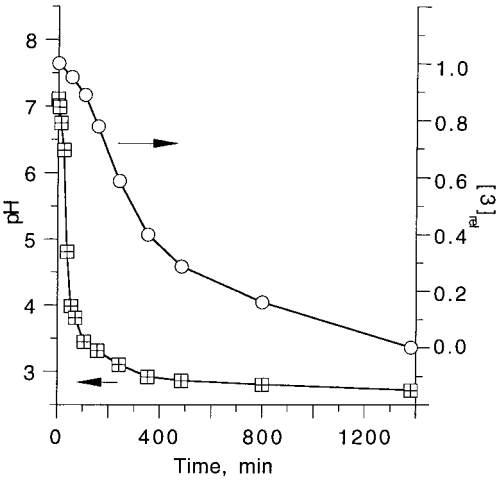

Figure 4. Unbuffered degradation of 4-chlorocatechol **3**. Relative concentration of **3** (circles) and pH of the mixture (crossed boxes). The pH of a dark (control) solution dropped linearly from 7.0 to 5.0 over the same time period.

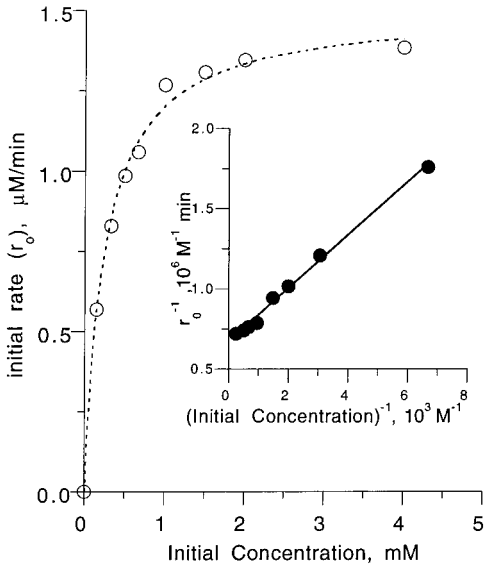

Figure 5. Initial rate of degradation of **3** versus initial concentration. Experiments were performed in a thermostatically controlled water-jacketed Pyrex cell at 30 ± 0.5 °C. Aside from temperature and concentration, standard conditions were used.

It has been reported that certain anions inhibit photocatalytic degradations.[42] Phosphate reduced the rate of oxidation of salicylic acid and aniline, for instance.[43] A similar effect was not observed here for **1**, **3**, or **7**, though the unbuffered data were necessarily less quantitative because of the need to manually regulate the pH by addition of hydroxide.

The effect of concentration of **3** on its degradation rate was also investigated over the range of 150−4000 μM using otherwise standard conditions and a fixed temperature of 30 °C. The results are shown in Figure 5. The inset shows a linearization of the rates following a Langmuir−Hinshelwood type relationship given in eqs 1 and 2, where k is a rate constant and K is an equilibrium adsorption constant. The values obtained for k and K are 1.5 μM min^{-1} and 4.0×10^4 M^{-1}, respectively. The dotted line in the main figure represents the rates calculated using the parameters obtained from the linearization.

$$r_0 = \frac{kKC_0}{1 + KC_0} \quad (1)$$

$$\frac{1}{r_0} = \frac{1}{k} + \frac{1}{kKC_0} \quad (2)$$

The early stages of degradation of **3** under standard conditions were dominated by formation of **5** and **7**. However, **5** degrades ($k = 0.031$ min^{-1}) more rapidly than **3** ($k = 0.013$ min^{-1}), so an exact branching ratio was not determined. These are the facile dark oxidation products of **4** and **6**, and it is quite likely that these latter two are actually the primary products. Solutions of **4** or **6**, analyzed by HPLC, invariably led to detection of **5** or **7**, respectively, even when solutions were prepared with argon-flushed water. The maximum concentration of **7** (ca. 0.25 mM) was 3-fold greater than that of **5**.

For further determination of the identities of degradation intermediates of 4-chlorocatechol, GC−MS detection was used. For these experiments, the standard initial concentration was 200 μM. Under acidic conditions, the acyclic compounds disappeared at about the same rate as **3**, but at neutral pH their decay was slowed and the maximum concentrations were generally higher. Thus the neutral pH was used. To avoid the use of buffer, the pH was maintained at 7.0 ± 0.5 by manual addition of NaOH solution during the photolysis. After a fixed period of time, optimized for having the greatest concentration and number of compounds present, the degradations were stopped. Attempts at direct analysis of dehydrated samples were unsuccessful. As a result, the compounds were silylated before GC analysis. Both alcohols and acids are functionalized. Repeat runs were made in which the reaction mixture was reduced with $NaBH_4$ or $NaBD_4$ prior to silylation. The resulting peaks, their ion trap mass spectra, and confirmed or proposed structures are given in Table 2. All of the compounds except those proposed for peaks 21, 26, 27, 29, 35, and 36 were confirmed by comparison to authentic samples. Structures for these latter peaks are based on the mass spectra and certain chemical arguments laid out below. This is not a complete list of intermediates in the degradation; a few very small peaks in the GC traces did not yield sufficient mass spectral data, and a few compounds may not have survived the analytical regimen. Additionally, a single large peak (37) was observed that was not identified. However, it appeared to be a compound with more than six carbons, presumably an adduct of **3** and a smaller intermediate. Further details are given in the Experimental Section.

Photocatalytic Degradation of 5-Chloro-2-hydroxybenzoquinone 7. In the degradation of **3**, **7** is one of the major early intermediates. Therefore its degradation was pursued to observe further downstream products. Samples of **7** are straightforwardly obtained by bubbling solutions of **6** with O_2.

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Table 2. Intermediates Detected in Degradations of 3, 7, and 10[a]

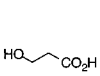
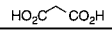
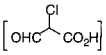
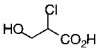
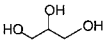
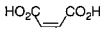
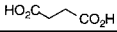
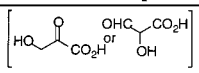
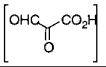
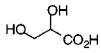
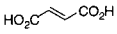
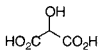
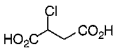
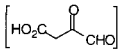
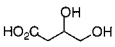
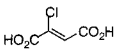
Peak	3	7	10	Intermediate[b]	Reduced intermediate	RT[c]	FW[d]	m/z values (relative abundance)
1	M	M	S	[OHC-CHO]	$HOCH_2CH_2OH$	8.01	206	**$NaBH_4$**: 73(40), 147(100), 103(10), 191(30) **$NaBD_4$**: 73(50), 103(10), 104(8), 147(100), 191(4), 193(5)
2	M	M	-			8.58	234	**$NaBH_4$**: 73(65), 93(20), 117(32), 133(10), 147(100), 190(20), 191(30), 219(13) **$NaBD_4$**: 73(75), 93(10), 117(20), 118(18), 133(10), 147(100), 190(15), 192(30), 220(12)
3	M	M	L	[OHC-CO_2H]	$HOCH_2$-CO_2H	9.17	220	**$NaBH_4$**: 73(60), 90(14), 103(10), 133(8), 147(100), 177(20), 205(24), 220(3) **$NaBD_4$**: 73(58), 103(8), 104(5), 133(12), 147(100), 177(12), 178(6), 205(13), 206(7)
4	L	L	L	HO_2C-CO_2H		9.58	234	73(56), 133(4), 147(100), 190(23), 219(29)
5	M	S	S			10.08	234	**$NaBH_4$**: 73(35), 103(4), 133(6), 147(100), 165(8), 177(24), 219(50) **$NaBD_4$**: 73(50), 104(6), 133(8), 147(100), 165(8), 178(18), 220(42)
6	L	L	M			10.49	248	73(29), 147(100), 217(4), 233(16), 248(2)
7	S	S	S			11.12	268	**$NaBH_4$**: 73(90), 102(20), 116(15), 147(100), 151(10), 152(4), 191(20), 193(6), 225(23), 227(8), 253(10), 255(4) **$NaBD_4$**: 73(60), 103(22), 117(10), 147(100), 152(10), 154(4), 226(20), 228(6), 254(8), 256(3)
8	S	S	-			11.44	308	**$NaBH_4$**: 73(100), 102(18), 103(10), 133(25), 147(90), 163(16), 205(5), 219(12), 235(35), 263(10), 293(5) **$NaBD_4$**: 73(86), 103(8), 104(6), 133(15), 147(100), 207(8), 221(10), 296(4)
9	M	S	S			11.54	260	73(45), 75(15), 133(7), 147(100), 171(16), 215(3), 245(13), 260(12)
10	M	-	-			11.58	262	73(30), 129(8), 147(100), 172(8), 247(28), 262(3)
11	M	M	M	 and 		12.07	322	**$NaBH_4$**: 73(100), 103(13), 117(18), 133(24), 147(70), 189(54), 205(10), 217(8), 292(55), 307(15) **$NaBD_4$**: 73(100), 102(18), 103(16), 104(10), 119(10), 133(20), 147(60), 190(35), 191(40), 207(8), 293(63), 309(18), 324(2)
12	L	M	S			12.22	260	73(55), 75(8), 143(58), 147(44), 171(8), 217(10), 245(100)
13	M	L	-			12.41	294	73(50), 147(100), 169(4), 205(5), 226(4), 249(4), 279(20), 281(7)
14	M	L	L			12.43	336	73(55), 102(15), 133(20), 147(80), 221(5), 293(55), 321(12)
15	S	S	-			12.51	296	73(80), 129(12), 147(100), 217(25), 245(20), 281(17), 283(6)
16	S	S	-			13.06	336	**$NaBH_4$**: 73(100), 101(12), 103(7), 117(6), 129(10), 133(15), 147(36), 157(8), 189(20), 191(8), 202(12), 203(10), 205(8), 231(20), 233(15), 246(8), 247(8), 321(22) **$NaBD_4$**: 73(100), 102(10), 103(8), 104(9), 117(5), 118(10), 133(12), 147(45), 159(8), 190(20), 191(12), 192(12), 203(8), 204(15), 205(8), 233(14), 234(15), 247(6), 248(8), 323(14)
17	M	M	M			13.30	294	73(80), 93(25), 127(28), 147(23), 171(5), 205(6), 250(5), 279(100), 281(35)

Table 2. (Continued)

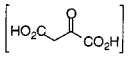
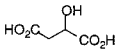
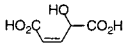
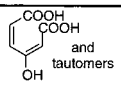
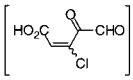
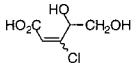
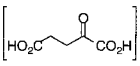
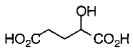
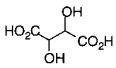
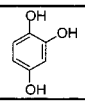
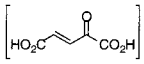
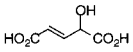
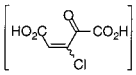
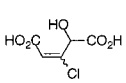
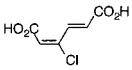
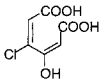
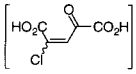
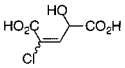
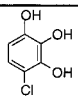
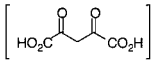
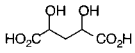
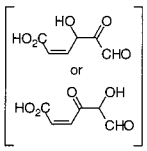
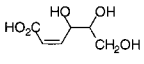
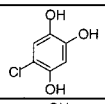
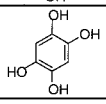
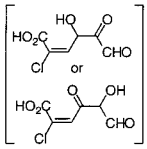
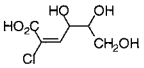
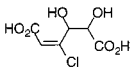
Peak	3	7	10	Intermediate[b]	Reduced intermediate	RT[c]	FW[d]	m/z values (relative abundance)
18	M	L	M			13.36	350	**NaBH$_4$**: 73(100), 101(12), 133(20), 147(80), 175(11), 189(8), 233(56), 245(22), 307(7), 335(16) **NaBD$_4$**: 73(100), 102(10), 133(20), 147(50), 176(6), 190(12), 234(10), 246(10), 308(18), 336(15)
19[e]	S	S	-			14.01	362	**NaBH$_4$**: 73(100), 133(12), 147(38), 156(18), 245(8), 303(8), 318(20), 347(12) **NaBD$_4$**: 73(100), 133(10), 147(45), 157(25), 246(8), 304(10), 319(22), 348(12)
20	M	-	-			14.21	374	73(80), 133(8), 147(30), 169(8), 241(10), 257(100), 330(25), 331(40), 359(26)
21	-	S	M			14.22	382	**NaBH$_4$**: 73(100), 103(20), 133(8), 147(35), 167(5), 176(6), 190(20), 192(8), 203(6), 277(12), 279(12), 303(7), 331(3), 352(30), 354(12), 367(12), 369(4) **NaBD$_4$**:73(100), 103(10), 104(8), 133(10), 147(50), 167(10), 177(3), 191(8), 204(5), 279(10), 281(8), 305(15), 333(10), 353(5), 369(12), 371(4)
22	M	S	-			14.25	364	**NaBH$_4$**: 73(100), 129(22), 147(40), 203(10), 247(16), 321(10), 322(20), 349(20) **NaBD$_4$**:73(100), 130(22), 147(50), 158(14), 204(150), 248(20), 322(8), 350(35)
23	S	S	M			14.29 and 14.50	438	73(100), 102(6), 133(10), 147(50), 189(15), 219(10), 292(30), 305(10), 333(8), 423(8)
24	S	-	-			14.38	342	73(60), 147(10), 211(8), 239(60), 254(10), 327(10), 342(100)
25	M	S	-			14.43	362	**NaBH$_4$**: 73(100), 113(15), 133(10), 147(48), 156(8), 245(10), 291(15), 303(8), 319(20), 347(45) **NaBD$_4$**: 73(100), 133(10), 147(45), 157(25), 246(8), 304(12), 319(22), 348(40)
26[f]	S	L	S			14.46 14.55	396	**NaBH$_4$**: 73(100), 127(15), 147(40), 167(10), 190(10), 241(6), 279(10), 281(4), 352(25), 353(20), 354(18), 355(8), 381(14), 383(5) **NaBD$_4$**: 73(100), 128(8), 147(35), 167(8), 191(10), 242(8), 280(8), 282(3), 353(20), 354(21), 355(15), 356(8), 382(12), 384(4)
27	S	-				15.08	320	73(100), 93(15), 123(25), 147(98), 187(10), 189(4), 203(70), 205(24), (230(10), 241(10), 261(8), 263(3), 285(50), 305(20), 307(7), 320(4), 322(2)
28	S	M	-			15.13	408	73(60), 93(15), 133(24), 147(30), 167(15), 169(5), 203(5), 275(5), 291(100), 293(35), 329(18), 349(20), 351(7), 373(24), 393(22), 395(7)
29[f]	-	S	-			15.18	396	**NaBH$_4$**: 73(100), 129(10), 133(12), 147(45), 167(10), 190(10), 241(6), 279(8), 281(3), 353(10), 355(3), 381(12), 383(4) **NaBD$_4$:** 73(100), 128(8), 133(8), 147(35), 167(8), 191(10), 266(15), 268(6), 280(6), 282(3), 353(30), 354(25), 355(20), 356(15), 382(12), 384(4)
30	S	-	-			15.20	376	73(100), 147(12), 179(10), 237(15), 273(95), 275(31), 361(10), 363(4), 376(55), 378(20)
31	M	L	-			15.21 15.27	452	**NaBH$_4$**: 73(100), 102(8), 133(16), 147(30), 217(18), 245(10), 292(40), 319(20), 437(20) **NaBD$_4$**: 73(100), 103(5), 133(10), 147(35), 218(5), 247(35), 293(15), 321(25), 439(12)

Table 2. (Continued)

Peak	3	7	10	Intermediate[b]	Reduced intermediate	RT[c]	FW[d]	m/z values (relative abundance)
32	S	-	-			15.31	450	**NaBH$_4$**: 73(100), 133(13), 147(40), 163(10), 191(10), 203(5), 217(15), 218(14), 243(10), 291(10), 317(12), 345(5), 435(20) **NaBD$_4$**: 73(100), 104(5), 133(10), 147(45), 207(5), 219(16), 244(15), 245(15), 292(5), 319(10), 335(8), 347(6), 437(12)
33	L	-	-			15.41	376	73(95), 147(12), 179(15), 237(55), 273(20), 275(6), 361(6), 363(3), 376(100), 378(40)
34	S	S	-			15.53	430	73(45), 147(15), 179(8), 207(8), 254(5), 342(10), 415(5), 430(100)
35	-	S	-			16.22 16.37	484	**NaBH$_4$**: 73(100), 102(5), 133(8), 147(25), 169(18), 189(5), 217(12), 292(10), 331(30), 332(15), 333(10), 343(15), 345(5), 350(18), 358(50), 379(10), 405(8), 407(10), 409(4), 433(6), 435(6), 469(10), 471(4) **NaBD$_4$**: 73(100), 103(5), 133(8), 147(25), 170(10), 191(5), 217(10), 293(15), 332(30), 333(16), 334(7), 344(15), 346(5), 359(40), 361(12), 381(6), 407(10), 409(12), 411(4), 435(4), 437(4), 471(8), 473(3)
36	-	-	M			16.43 16.49	498	73(100), 102(8), 117(22), 133(10), 147(40), 190(10), 219(8), 221(10), 279(25), 281(10), 292(30), 352(15), 354(6), 365(18), 367(7), 373(28), 393(5), 395(2), 455(5), 457(2), 483(10), 485(4)
37[g]	L	-	-		unknown[g]	17.31	402	73(100), 117(10), 147(20), 168(10), 185(5), 200(5), 227(5), 241(25), 271(5), 285(50), 387(5), 402(10)

[a] All compounds observed as the TMS derivatives. Photoreaction conditions: Initial concentration of substrate 0.2 mmol, pH 7.0 volume = 100 ml. TiO_2 = 0.5 g L^{-1}, photolysis time = 240, 120 and 80 min for **3**, **6** and **10**, respectively. Peaks are qualitatively listed as "small," "medium," or "large" from each precursor. [b] Compounds shown in brackets were not observed without reduction, but are the precursors to the "reduced intermediates." Compounds observed without reduction were also observed with reduction. [C] Times are given in the format of Min.Sec. A 30 m DB5 column was used with the following temperature program: 50 °C for 4 minutes, followed by a ramp up to 280 °C at 15 °C/min, and holding at the final temperature for 5 min. [d]From CI run. [e] The silylated derivative of the unreduced compound is not stable, and this peak is rather small.[39] The retention time is for the silylated reduced compound. [f]See text for a discussion of the distinction between peaks 26 and 29. [g] See Experimental Section for discussion.

As observed for benzoquinone[44] and hydroxybenzoquinone,[39] **7** is reduced to **6** under photocatalytic treatment. In general, HPLC and GC analyses disagreed on the relative amounts of these two compounds in solution, with HPLC showing more of the quinone than did GC. It can be reasonably assumed that there is a steady-state concentration of **6** in degradations of **7**, and in fact, we will suggest below decomposition mechanisms that go via **6** in that the major oxidizing species, $HO^{\bullet}_{ads}$ and h^{+}_{VB}, are electrophilic reagents.

In dark control experiments, a single HPLC peak that remains unidentified was produced. Under standard conditions, a small amount of this same compound was observed by HPLC, but it was quickly degraded photocatalytically. The photocatalytic reaction was substantially faster than the dark reaction. No known cyclic compounds were observed by HPLC—only the usual mix of acyclic acids. They are noted in Table 2. With 2-propanol added, the rate of degradation of **7** is reduced by about a factor of 7 (Table 1), and the amount of the dark intermediate increases because of the lack of competition in its formation and lack of degradation.

Photocatalytic Degradation of 4-Chloropyrogallol 8. A small quantity of **8** is observed in the photocatalytic degradation of **3**. Degradation of **8** in the dark is complete within 2 h, and at least 10 intermediates can be detected by HPLC. The dark reaction is relatively fast and is clearly competitive with photocatalytic degradation. GC—MS traces are nearly the same from ordinary or dark degradations, and the resulting compounds are mostly different than those from degradation of **3**. This confirms that formation of **8** is a relatively minor process for **3**.

Discussion

Kinetics of Degradation. The Langmuir—Hinshelwood (LH) behavior of the decay kinetics of **3** merits brief discussion. It is widely recognized that the rate constant k obtained from these plots is entirely dependent on the experimental setup. In the early applications of the LH equation to this sort of data, the equilibrium constant K

(44) Richard, C. *New J. Chem.* **1994**, *18*, 443—445.

was considered strictly related to the binding constant between the organic substrate and the TiO_2. It has since become clear that this connection is tenuous at best; in the context of arguments over whether binding is necessary for reaction, it has been shown that several reasonable kinetic schemes, some of which do not include substrate binding to the oxide, lead to the same kinetic form.[45] Indeed, the measured *K* values for 4-chlorophenol routinely exceed the dark binding coefficients.[19,21,24]

The observed values of *K* are, of course, dependent on conditions, but the value established here (40 mM^{-1}) exceeds any of the reported values for 4-chlorophenol of which we are aware. It is also known that 4-chlorocatechol binds to TiO_2 much more strongly than does either hydroquinone or 4-chlorophenol.[28] (It is reasonable to hypothesize from the adsorption data that this is a general property of structures with *ortho* hydroxy groups.[46−48]) In a careful kinetic study using oxygen-free conditions and a TiO_2 photoelectrode, Kesselman showed that the rate of degradation of **3** was proportional to the amount adsorbed on the TiO_2.[49] From IR experiments, they determined a binding constant of 97 mM^{-1} at pH 5, a value of the same order of magnitude as *K* measured here at pH 7. Nonetheless, the data here do not directly address the significance of the measured *K*.

The effect of pH on photocatalysis rate and/or efficiency is depends on the substrate,[30,38,42,49−53] but a correlation can be made in this case between the rates and substrate adsorption. The pH of zero charge for TiO_2 is widely quoted to be about 6.4.[42,46] Above this, there is a net negative charge, and below there is a net positive charge on the titanium dioxide particle, which can affect adsorption. The pK_a values of 4-chlorocatechol are 8.8 and 12.7. At 0.5 mM concentration of **3**, Martin and co-workers observed a maximum in total adsorption to TiO_2 over the pH range of approximately 7.5−10.[46] Below about 50 μM, the binding is bidentate−binuclear, i.e., the O atoms are independently adsorbed to Ti atoms, whereas at the concentrations used here, nonspecific adsorption is also expected. The observed dependence of the initial rate of degradation of **3** qualitatively follows the pattern of the adsorption measured by Martin[46] and thus may reflect better hole-trapping efficiency. The initial rates of degradation on the Martin photoelectrode with applied bias voltage also showed an increase with pH, but the effect was more modest.[49] The conditions of their experiment (immobilized photoelectrode, 10 mM KCl, N_2 purge, 50 μA constant current) are sufficiently different that parsing the quantitative differences in behavior is probably not warranted.

The issue of surface reactions is ambiguously addressed by the experiments using 2-propanol as an additive. The ambiguity comes about because the role of the 2-propanol cannot at present be perfectly delimited. Previously, the technique has been interpreted in terms of discriminating between direct (hole) oxidation and reaction with $HO^{\bullet}$.[54] The high concentration used (ca. 130 mM) is expected to be sufficient to scavenge virtually all diffusing hydroxyl radicals[54,55] but may also compete for surface reactions, despite the low binding constant of 2-propanol. We have found in unpublished work that, at this concentration level, it has a measurable but not overwhelming effect on adsorption by compounds such as these. In the current results, all of the degradations are significantly inhibited by the addition of the alcohol. The level of inhibition observed for **3** is in line with previous workers' observations using ZnO as the photocatalyst.[55]

Although further investigations into the use of alcohols in photocatalytic conditions and the mechanisms of their action are clearly justified if they are to become a truly diagnostic technique, the most intriguing result reported here is that some degradations are inhibited more than others. We offer speculation as to the origin of this effect. The photocatalytic oxidation of hydroquinone is nearly completely inhibited, though that of 4-chlorophenol, another poorly binding substrate, is not. However, it need not be that hydroquinone is actually unreactive under these circumstances, only that it is not hydroxylated to benzenetriol. If hydroquinone is oxidized to the semiquinone or benzoquinone level instead, it can quickly be reduced back by acting as an electron sink for conduction band electrons.[39,44] Thus this result is consistent with the trapping of hydroxyl radicals (free or surface-bound) by 2-propanol, regardless of whether hydroquinone undergoes surface-bound one-electron oxidations. 4-Chlorophenol has no such "reversible" reaction, perhaps explaining its continued reactivity in the presence of 2-propanol despite poor binding. Stafford has pointed out[33] that photocatalytic degradations of **1** that have generated larger amounts of hydroquinone than chlorocatechol have been carried out under conditions where surface chemistry was probably favored. The current results suggest an exacerbating effect; chlorocatechol is probably selectively degraded under such conditions. (Alcohol additives have also been used to generate reducing conditions for nitroaromatics and certain halogenated compounds; that chemistry does not appear as relevant to the current case. See, for instance, references 56−58.)

Degradation Pathways. As shown in Scheme 1, 4-chlorophenol is converted to a mixture of hydroquinone and 4-chlorocatechol. The degradation of hydroquinone was the subject of Part 1 of this work.[39] Its first step is the almost quantitative formation of 1,2,4-benzenetriol (**4**), and much of that paper was based on analysis of the degradation of that compound. In the same way, the heart of the intermediate study here is based on the degradation of 4-chlorocatechol **3**. Here there is a greater choice of first steps. One of them is to form **4**, whose degradation is already outlined. The HPLC traces represented in Figure 3 give the sum of [**4**] and [**5**] as $[\mathbf{5}]_{obs}$ because of dark oxidation; the analogous coupling is

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(46) Martin, S. T.; Kesselman, J. M.; Park, D. S.; Lewis, N. S.; Hoffmann, M. R. *Environ. Sci. Technol.* **1996**, *30*.
(47) Terzian, R.; Serpone, N.; Minero, C.; Pelizzetti, E.; Hidaka, H. *J. Photochem. Photobiol., A* **1990**, *55*, 243−249.
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(49) Kesselman, J. M.; Lewis, N. S.; Hoffmann, M. R. *Environ. Sci. Technol.* **1997**, *31*, 2298−2302.
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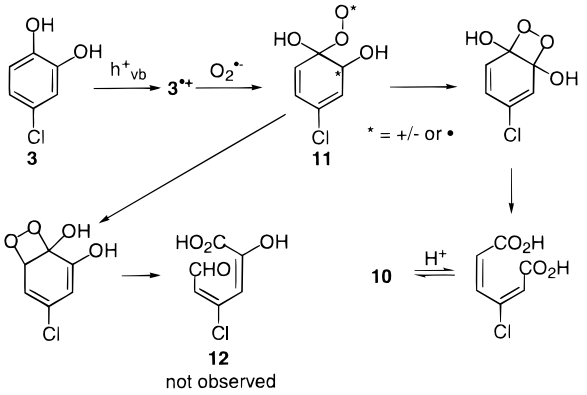
(53) Tang, W. Z.; Huang, C. P. *Water Res.* **1995**, *29*, 745−756.
(54) Richard, C.; Boule, P. *New J. Chem.* **1994**, *18*, 547−552.
(55) Sehili, T.; Boule, P.; Lemaire, J. *J. Photochem. Photobiol., A* **1989**, *50*, 117−127.
(56) Ferry, J. L.; Glaze, W. H. *Langmuir* **1998**, *14*, 3551−3555.
(57) Calza, P.; Minero, C.; Pelizzetti, E. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3765−3771.
(58) Ohtani, B.; Kakimoto, M.; Miyadzu, H.; Nishimoto, S.; Kagiya, T. *J. Phys. Chem.* **1988**, *92*, 5773−5777.

Scheme 2



observed for **6** and **7**. Because of the known efficient photocatalytic reduction of benzoquinone to hydroquinone and the related examples observed here, we assume for purposes of this discussion that most of the chemistry of these two redox couples occurs from **4** and **6**. However, the quinone forms cannot be absolutely ruled out.

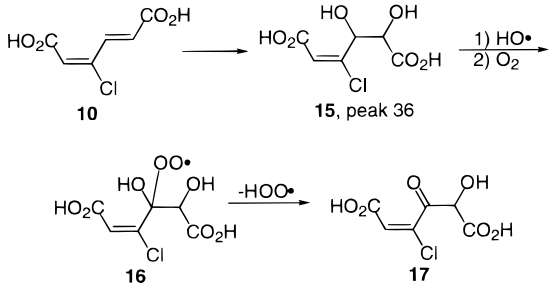
Four products are observed that derive directly from **3**. They are two hydroxylation products **6** and **8**, the substitution product **4**, and the cleavage product **10**. Although **8** degrades quickly either in the dark or with light and so it is harder to quantify the amount that is made, the products from its degradation are inconsistent with degradation of **3**. As a result, its small peak size is taken at face value, and this is assigned as a minor pathway. The other hydroxylation product **6** is a very large peak in the GC traces; the corresponding quinone is the largest in the HPLC traces and is assigned to be the major product. It is presumed that all of these but **10** are the products of reaction of **3** with HO• or its surface-bound equivalent. By comparison to **4** and **6**, the first step of degradation of **3** leads to much more hydroxylation (i.e., smaller fraction of cleavage). This is understandable on the basis of their respective oxidation potentials, suggesting that the selectivity for hydroxylation versus cleavage is driven by more than just having good binding affinity.

The pathway of degradation from 1,2,4-benzenetriol has been discussed.[39] The principal products of its degradation are ring-opened compounds, shown as peaks 20 and 32.

The degradation pathways of **6** and **10** will now be discussed. The opening of **6** to form **10** is consistent with one-electron oxidation followed by trapping with superoxide (Scheme 2), as we have argued in the accompanying paper. Intermediate **11** could potentially close to give two dioxetanes, but **12** is not observed. However, this is consistent with the position of the hydroxy group that tends to localize charge and/or spin adjacent to it, thus favoring closure on that side. An endoperoxide formed by 1,4-closure of **11** is also a possibility. After rupture, this would lead to a two-carbon fragment and maleic acid or ketosuccinic acid, which are observed as peaks 9 and 18, respectively. However, other reasonable pathways also exist to get to these compounds.

Protonation is another potential variable. For instance, the 4-chlorocatechol that is specifically bonded to the TiO_2 in the manner of Martin's work[46] will be deprotonated throughout the reaction and will produce the bound dianion of the diacid, whereas most of the nonspecifically bound material is diprotonated, on the basis of the pH of the solution, but may deprotonate after loss of an electron.

Scheme 3



The stereochemistry of **10** is different than one would expect from Scheme 2. However, it is known that (2*E*,4*Z*)-3-chloromuconic acid isomerizes to **10** extremely easily in acidic water.[59,60] The workup used here briefly exposed the compounds to acidic conditions; the isomerization may occur either during the photolysis or as a result of the acidic workup.

Degradation of **10** was also carried out, as shown in Table 2. Peak 36 represents dihydroxylation of the C4–C5 π-bond. The mechanism of this is still unclear, but it was previously observed for related compounds, including maleic acid.[39] No other six-carbon compounds are observed. Peaks 26 and 29 are isomeric, but of the two, only peak 26 is obtained from **10**. Peak 21 represents the only other five-carbon piece. Although the mass spectra do not lend themselves to easy assignments of the position of the chlorines in these compounds, there seems no reason to believe anything but that the C3 attachment in **10** is maintained, making the assignments 3-chloro-4,5-dioxopent-2-enoic acid (**13**) for peak 21 and both isomers of 3-chloro-2-oxopent-4-enedioic acid (**14**) for peak 26.

The pathways to get to these compounds are not further revealed by the current data. A reasonable first few steps are illustrated in Scheme 3, though alternatives clearly exist. Oxidation of **15** by hydroxyl ultimately gives **17**. The regiochemistry of the first step is unimportant, because **17** can tautomerize in aqueous solution. It, in turn, is subject to decarboxylation and further oxidation to give **13** and **14**.

At the four-carbon level, chlorofumaric acid, ketosuccinic acid, and tartaric acid are the most important peaks. Photo-Kolbe chemistry[61–64] on **14** may lead to chlorofumaric acid, which may in turn be the source of most of the rest of the peaks. This chemistry is too far removed from the starting materials here to be convincingly argued.

Degradation of **7** was also examined. For purposes of this discussion, it is again assumed that reduction to **6** is rapid with the lamps on and the chemistry proceeds from there. A small amount of substitution to form **9** is observed, but the largest peak derives from cleavage

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(60) Pieken, W. A.; W., K. J. *J. Org. Chem.* **1990**, *55*, 3029–3035.
(61) Sun, Y.; Pignatello, J. J. *Environ. Sci. Technol.* **1995**, *29*, 2065–2072.
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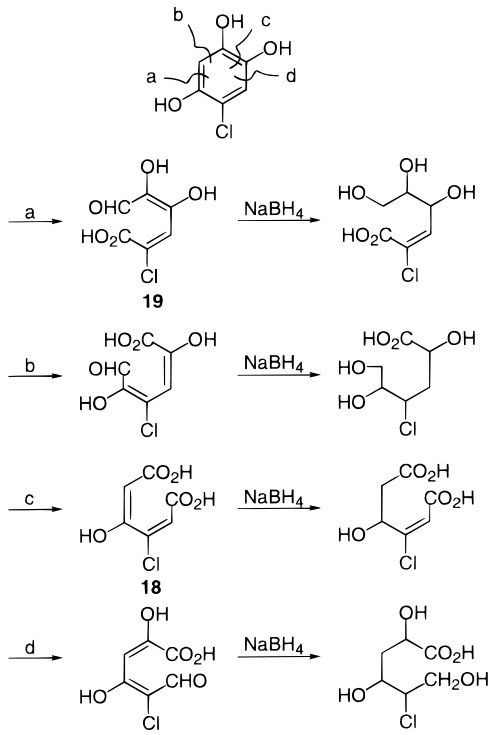
(64) Dixon, W. T.; Norman, R. O. C.; Buley, A. L. *J. Chem. Soc.* **1964**, 3625–3634.

Scheme 4



between the *ortho* hydroxy groups to give peak 28 ((*E*,*E*)-4-chloro-3-hydroxymuconic acid (**18**) and tautomers), confirmed by authentic sample.

An alternate cleavage is observed as small peak 35, which is a six-carbon compound only observed on degradation of **7**. In the absence of authentic samples, its assignment must be indirect. The $NaBD_4$ results indicate that two reducible groups are present, and the formula gives five oxygens and the chlorine. Analysis of the reasonable cleavages of **6** by means of the mechanism in Scheme 2 allows assignment of the peak as **19** (Scheme 4). Cleavage of bond a gives the compound assigned in the table and after reduction gives the correct observed product. Cleavage of bonds b or d gives compounds with the same formula but two too many hydrogens. Cleavage of c leads to the major observed cleavage product, peak 28.

Numerous five-carbon compounds are observed on degradation of **7**. The two main ones are 2,4-dioxopentanedioic acid (**20**, peak 31) and 3-chloro-2-oxopent-3-enedioic acid (**14**, peak 26). Compound **20** is likely to derive from straightforward degradation of **18**. Attributing **20** is somewhat more difficult in that it has undergone dechlorination. Photocatalytic dechlorination is well known (see, for instance, references 65 and 66), but another reasonable suggestion can be made. Compound **19** (as drawn and most tautomers) is a vinylogous acid chloride. As a result, hydrolysis should be relatively facile to produce the enol. At that point, straightforward oxidation chemistry can be written to get to **20**. Alternatively, it is possible that **20** derives from **9**. We view this as less likely because the trioxygenated benzenes readily cleave, and we suggest that the peak for **9** (peak 34) is small because little of it is produced. No new chemical ideas need to be invoked to suggest routes for the smaller five-carbon peaks.

Summary and Conclusions

The TiO_2-mediated photocatalytic degradation of 4-chlorophenol has been studied from the perspective of identifying the chemical pathways involved in its mineralization. The well-established first step produces both hydroquinone and 4-chlorocatechol. The previous paper in this series and this one examine the degradation pathways of these two compounds, respectively. In Scheme 5 is shown a summary of the most reliable connections made from 4-chlorophenol to the five-carbon stage. Simple dihydroxylations have been omitted for clarity. Undoubtedly other connections exist (some minor five-carbon compounds are not even included), but we believe the pathways as written to be reliable.

Over the course of this work, all of the observed six-carbon acyclic compounds were consistent with a single general mechanism for ring cleavage in which the first microscopic step is single-electron oxidation of the substrate. We have proposed that the radical cation is trapped by superoxide and that a resulting dioxetane is responsible for C−C cleavage. Although hypothetically possible for any of the cyclic substrates, the ring-cleavage reaction is only truly competitive with hydroxylation reactions when *ortho* hydroxy groups are present on the ring, particularly so when the ring is thrice oxygenated. Two major rationalizations for this exist, both of which probably contribute: (a) the *ortho* dihydroxy arrangement is superior for adsorption to the TiO_2, making single-electron transfer to h^+_{VB} more likely, and (b) the more highly oxidized structures have inherently lower oxidation potentials, making electron transfer more favorable. The reported results are all consistent with much of the degradation chemistry occurring at the surface of the TiO_2 particle.

On the basis of previous workers' studies in photocatalysis, radiolysis, and homogeneous photolysis of aqueous hydrogen peroxide solutions, speculative degradation pathways from the acyclic six-carbon compounds to most of the five- and four-carbon compounds have been proposed. The number of two-, three-, and four-carbon compounds and the multiple routes that might produce them prevent complete descriptions of the degradations without further work. A summary of the overall proposed paths is given as Scheme 5.

Experimental Section

Degradation Reactions; General Conditions. Solutions were prepared using water from a Millipore Milli-Q Plus purifier. When buffered, solutions contained 5 mM sodium phosphate buffer at pH 7.0 unless otherwise indicated. Temperature was controlled to 26 ± 2 °C during photolysis by means of a fan. Standard conditions for HPLC analysis employed 100 mL solutions in a Pyrex vessel with 50 mg of TiO_2 and the desired organic compound at 2 mM. Each mixture was treated in an ultrasonic bath for 5 min to disperse larger aggregates, purged with O_2, and stirred for 15 min in the dark before the irradiation was started. The mixture was continuously purged with O_2 throughout the experiment. Irradiations were carried out in Rayonet mini-photochemical reactor with

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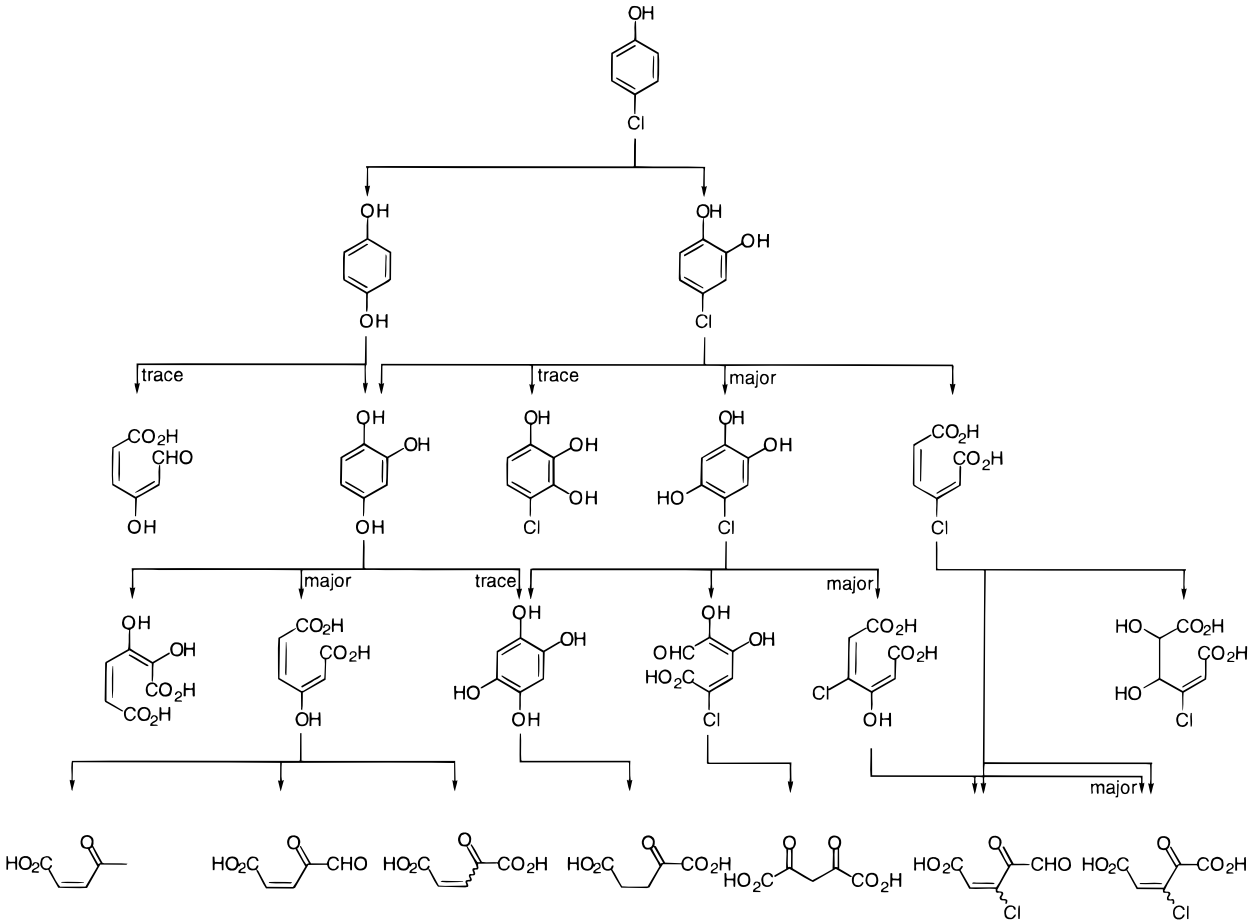
(66) Kenneke, J. F.; Ferry, J. L.; Glaze, W. H. The TiO_2-Mediated Photocatalytic Degradation of Chloroalkenes in Water. In *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier: New York, 1993; Vol. 3, pp 179−191.

Scheme 5



magnetic stirring and fan cooling to 26 ± 2 °C. Light was supplied by 8 × 4 W "black light" lamps whose broad emission is centered at 360 nm. For HPLC analysis, samples (0.5 mL) were withdrawn from the reaction vessel at regular time intervals during the irradiation. They were centrifuged using an Eppendorf 5415C and filtered using 0.2 μm Whatman cellulose nitrate syringe filters to remove TiO_2 before HPLC analysis. When temperature regulation was needed, a Pyrex vessel with an outer jacket was used and the temperature was regulated to 30.0 ± 0.5 °C by circulation of thermostatically controlled water.

HPLC Analyses. The concentrations of cyclic compounds **1**−**7** were measured by HPLC (HP 1050 with diode array UV−vis detector) using an ODS Hypersil C_{18} reverse-phase column (5μm loop, 200 mm × 2.1 mm). All substances were simultaneously detected by absorbance at 220, 255, and 285 nm, and response factors were obtained at the most favorable wavelength for each compound. The eluent was a mixture of methanol and water containing 0.2% acetic acid. The eluent was 10% methanol for the first 6 min. Then the concentration of methanol was increased to 40% methanol within 2 min, and this proportion is held until the analysis was finished. The flow rate was 0.5 mL min^{-1}. The identification of the intermediates by HPLC was performed by comparing the retention times and the UV spectra with those of authentic samples. The concentration of compounds that were not identified was roughly approximated using the equation derived from calibration measurements for the starting material from which the intermediate was produced. The concentration of acyclic intermediates was similarly estimated by comparing with the absorbance of oxalic acid.

Decay rate constants in Table 1 were determined by plotting the $\ln(conc/conc_0)$ vs. time for the first two to three half-lives, over which the decays fit well to this first-order treatment. No particular significance is attached to the absolute values. Dark decays were obtained using identical conditions as usual, other than the absence of light. Multiple runs of certain decays showed that rate constants were reproducible to better than 10%.

GC−MS Analyses. The standard conditions for solutions were modified when GC was to be used. Initial concentrations of the organics were 200 μM. Unbuffered solutions were used, and the pH was adjusted to the desired value ± 0.5 throughout the photolysis by periodic addition of NaOH. After the photolysis was completed, the entire mixture was acidified to pH 2.5 by addition of HCl. Solutions were freeze-dried and silylated as previously described.[39] Some solutions were treated with $NaBH_4$ or $NaBD_4$ prior to silylation as previously described.[39] GC analysis was done with a 25 m DB-5 column coupled to either a Finnigan Magnum ion trap mass spectrometer for MS analysis or an FID detector for routine work. It should be noted that ion trap mass spectra show intensity patterns different than those of EI−MS. The temperature program was 50 °C for 4 min and then ramp to 280 °C at 15 °C min^{-1}.

Materials. The following compounds were obtained from Aldrich at the highest purity available and used without further purification: 4-chlorophenol, ethylene glycol (peak 1), lactic acid (peak 2), glycolic acid (peak 3), oxalic acid (peak 4), malonic acid (peak 6), glycerol (peak 8), maleic acid (peak 9), succinic acid (peak 10), fumaric acid (peak 12), chlorosuccinic acid (peak 15), malic acid (peak 18), tartaric acid (peak 23), 1,2,4-benzenetriol (peak 24), 1,1,1,3,3,3-hexamethyldisilazane, chlorotrimethylsilane, pyridine, and sodium borohydride. Tartronic acid (peak 11) was provided by Sigma. The water employed was purified by a Milli-Q UV plus system (Millipore) resulting in a resistivity more than 18 MΩ cm^{-1}. TiO_2 is Degussa P-25 which consists of 75% anatase and 25% rutile with a specific BET surface area of 50 m^2 g^{-1} and a primary size of 20 nm.[67] NMR spectra were obtained at 300 (^1H) and 75 MHz (^{13}C) on a Varian VXR instrument.

Compounds were identified in GC−MS runs by comparison of the silylated sample retention times and fragmentation patterns with those of silylated authentic compounds. The compounds that correspond to peaks 5, 11, 14, 19, 20, 22, 31, 32, and 34 were prepared as previously reported.[39]

The following compounds were prepared by literature methods: 4-chlorocatechol, **3**;[68] 2-chloro-3-hydroxypropionic acid (peak 7);[69] chloromaleic acid (peak 13),[70] mp 107 °C, ^{1}H NMR (acetone-d_6): δ 6.52, ^{13}C NMR: δ 164.4, 163.7, 137.8, and 124.8; chlorofumaric acid (peak 17),[70] mp 192−193 °C, ^{1}H NMR (acetone-d_6): δ 7.27, ^{13}C NMR: δ 164.5, 162.8, 134.2, and 128.7; (*E*,*E*)-3-chloromuconic acid (peak 27);[59,60,71] 4-chloropyrogallol (peak 30),[72] mp 163−164 °C, ^{1}H NMR (acetone-d_6): δ 6.68 (d, J = 8.7 Hz, 1 H), 6.42 (d, J = 8.7 Hz, 1 H), ^{13}C NMR δ 145.7, 143.2, 135.1, 120.1, 112.4, 108.3.

Peak 28. (*E*)-3-Chloro-4-oxohex-2-enedioic Acid. A solution of HOAc (5 mL), HOOAc (32%, 2.52 mL, 12 mmol), and ferric acetate (1 mg) was stirred at room temperature. To this was added dropwise a solution of 5-chloro-1,2,4-benzenetriol (0.60 g, 3.7 mmol) dissolved in HOAc (10 mL) at approximately 1 drop per minute. After an additional 1 h, the reaction was concentrated under vacuum to give a dark residue (0.5 g). NMR analysis of the concentrated oil showed that (*E*)-3-chloro-4-oxohex-2-enedioic acid was the major component (>60%) of a mixture. Attempts to purify the compound by chromatography were not fruitful. Tituration of the mixture with acetone or chloroform confirmed the assignment of the ^{1}H NMR by changing identities and ratios of impurities but also did not result in pure material. In $CDCl_3$, the closed form, i.e., (3-chloro-2-hydroxy-5-oxo-2,5-dihydrofuran-2-yl)-acetic acid, predominates, whereas in acetone, the equilibrium favors the open form. ^{1}H NMR ($CDCl_3$): δ 6.24 (s, 1 H), 3.21 (d, J = 16.5 Hz, 1 H), 2.83 (d, J = 16.5 Hz, 1 H). ^{1}H NMR (acetone-d_6): δ 6.41 (s, 1 H), 3.12 (s, 2 H). ^{13}C NMR (75 MHz): δ 169.3, 167.5, 158.9, 120.2, 104.8 and 39.8.

Peak 33. 5-Chloro-1,2,4-benzenetriol (6).[73] 1,2,4-Benzenetriol (1.0 g, 7.9 mmol) was dissolved in dry ether (50 mL) in an ice bath. Sulfuryl chloride (1.1 g, 8.1 mmol) was added dropwise. The reaction was stirred in an ice bath for 24 h and then refluxed for 3 h. A black residue (1.2 g) was obtained on removal of solvent. The crude material was sublimed at 80−90 °C at 0.2 Torr, and the sublimate was recrystalized in benzene to give light brown crystals (0.82 g, yield 65%), mp 117 °C (d). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.87 ppm (s, 1 H), 6.61 (s, 1 H), 5.12 (two close singlets, 2 H, exchanges with D_2O), and 4.70 (s, 1 H, exchanges with D_2O). ^{13}C NMR (75 MHz): δ 147.0, 145.9, 139.6, 116.8, 110.1, and 105.0.

Compounds Tentatively Identified on the Basis of MS Pattern. The mass spectra, along with reasonable constraints based on the starting materials, generally give unique molecular formulas. The number of TMS groups is readily determined from the molecular weight and certain fragments. It corresponds to the total number of alcohol and acid sites in the unsilylated compound. If the compound is a reduction product, the number of aldehyde and ketone groups in the parent is given by the additional molecular weight when $NaBD_4$ is used. The names used below refer to the unsilylated compounds, just as in Table 2.

Peak 16. The identity of 3,4-dihydroxybutyric acid was confirmed by comparison to the reported mass spectrum of the silylated derivative.[74]

Peak 21. This compound has three acids and/or alcohols. A formula of $C_5H_7ClO_4$ is obtained. The parent has two aldehydes and/or ketone and four unsaturations; the derivative has two unsaturations. The assignment is made partly in analogy to peak 19 of Table 1 in our previous work.[39] On the basis of its appearance on degradation of **7** and particularly **10**, 3-chloro-4,5-dihydroxy-2-pentenoic acid is the most likely structure.

Peak 25. This compound is identical to peak 23 in Table 1 of our previous work.[39] It was assigned on the basis of having a mass spectrum identical to silylated *cis*-4-hydroxy-2-pentenoic acid but a different retention time.

Peak 26. This compound has three acids and/or alcohols. A formula of $C_5H_5ClO_5$ is obtained. The parent has one aldehyde or ketone and four unsaturations, and the derivative has three unsaturations. Both 2- and 3-chloro-2-pentenedioic acid are possible, but the 3-chloro isomer is chosen because of the appearance from degradation of **10**. The two peaks are presumed to be due to E/Z isomerization.

Peak 29. This compound is an isomer of peak 26. 2-Chloro-4-hydroxy-2-pentenedioic acid is proposed on the basis of the fact that it does not appear on degradation of **10**.

Peak 35. This compound has four acids and/or alcohols and a formula of $C_6H_9ClO_5$. The parent has two aldehydes and/or ketones and four unsaturations. The derivative has two unsaturations. The proposed structure is a straightforward degradation product of **6** (Scheme 4).[39] The two peaks are consistent with the two diastereomers of the alcohols but are also consistent with alkene stereoisomers.

Peak 36. This compound has four acids and/or alcohols. It is not reduced by $NaBH_4$ and has a formula of $C_6H_7ClO_6$. It has three unsaturations and is a simple derivative of 3-chloromuconic acid. Dihydroxylation of fumaric acid and related compounds was observed previously.[39] The two diastereomers are again consistent with the hydroxyl groups.

Peak 37. This compound was only observed on photocatalytic degradation of **3**. The mass of the silylated compound is 402. The large peak at 285 (i.e., loss of 117) is usually correlated with a CO_2TMS group. Both 402 and 285 contain a single Cl atom, as indicated by the isotope pattern. This compound is not reduced by $NaBH_4$. Several possible formulas can be written; perhaps the most reasonable is $C_{10}H_5O_6Cl(TMS)_2$, corresponding to $C_{10}H_7O_6Cl$ in the parent. If the reaction mixture from degradation of **3** is worked up by reduction of the aqueous volume and ether extraction, followed by direct analysis, only two GC−MS peaks are observed. They correspond to **3** and a compound with the following MS: 220(30), 205(100), and 177(25). This ether extract can be silylated to produce a mixture whose principal components are silylated **3** and peak 37. To the extent that the correlation can be made between peak 37 and the 220-mass (unsilylated) peak, there is an upper limit of two TMS groups on peak 37. With this assumption, peak 37 must be a compound with more than six carbons and thus an adduct between **3** and some other compound. This is consistent with peak 37 not being observed in any of the other degradations analyzed by GC−MS reported in this paper.

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Supporting Information Available: Copies of proton NMR spectra from the preparation of authentics samples for peak 28 in acetone and chloroform. This material is available free of charge via the Internet at http://pubs.acs.org.

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