Photocatalytic Degradation of 4-Chlorophenol. 1. The Hydroquinone Pathway

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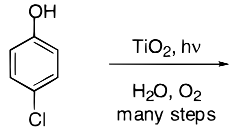
Complete mineralization of 4-chlorophenol in water can be achieved by photocatalytic degradation of oxygenated solutions containing suspended TiO_2. The chemical pathways of this degradation are complex, and in this paper, that which begins with hydroquinone is examined. Hydroxylation to form 1,2,4-benzenetriol is the first step, though a very small amount of cleavage of the C1−C2 bond is observed. The first major group of acyclic compounds derives from oxidative cleavage of either the C1−C2 or C3−C4 bond of 1,2,4-benzenetriol. It is argued that this results from single electron oxidation and capture by superoxide. Many smaller compounds have also been identified, and routes to various ones of them are proposed. Nearly all of the compounds are verified by use of authentic samples.

Introduction

Photocatalytic degradation of organic pollutants in oxygenated water by TiO_2 or other semiconductors belongs to a class of water reclamation strategies known as advanced oxidation processes.[1−3] It is well established that with exhaustive treatment virtually all organic compounds are “incinerated” or “mineralized” to H_2O, CO_2, and other inorganic ions. Among the oxidative species that are formed under the reaction conditions are surface-bound and perhaps free hydroxyl radicals, hydroperoxyl and other peroxyl radicals, valence-band holes in TiO_2, and hydrogen peroxide. Most of the oxidative activity is attributed these species.

Among the types of organics that have been most extensively investigated as targets for photocatalytic degradation are halogenated organics, both aliphatic and aromatic. Of these, 4-chlorophenol[4] has become a standard for evaluating various experimental parameters for photocatalysis.[4−28] Despite its ubiquity in this literature, almost nothing is known about the chemical degradative steps beyond the first two. The focus of this and the accompanying paper is to identify the stable intermediates in the photocatalytic degradation of 4-chlorophenol, with particular focus on the important ring-opening steps. From these products, some inferences may be drawn about the microscopic chemical processes, but direct detection of radicals and radical ions has not been carried out here.



The intermediates in the earliest stages of the degradations of a number of aromatic compounds have been reported,[29−45] including those from 4-chlorophenol and

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several closely related derivatives.[4,6,12,14−16,21,46−51] From a fundamental perspective and because real applications of photocatalytic techniques, particularly those that take advantage of natural sunlight, may result in incomplete degradation, it is necessary to investigate further the degradation pathways. Some intermediate compounds could potentially be as or more toxic than the initial pollutants.[52] Moreover, the chemical outcomes of various steps may help reveal the detailed physical processes that have been investigated and debated over the years by other techniques.

Although the initial steps of the degradations of various aromatic compounds are known, the nonaromatic and acyclic intermediates generally are not. We are aware of only a few studies in which any ring-opened products are discussed.[31] In the degradation of *p*-dimethoxybenzene, the methyl esters of maleic and fumaric acid were identified.[33] In the same study, *m*-dimethoxybenzene and *o*-dimethoxybenzene yielded the intermediates shown in Figure 1. The dimethoxy compounds were chosen in favor of the corresponding hydroquinones because they eased the analytical difficulties associated with isolating and identifying highly oxidized, water soluble, aliphatic species. Olivé and co-workers briefly report the degradation of 1,2,4-benzenetriol and published the observation of muconic acid, butadiene, and fumaric acid in GC−MS runs (Figure 2).[41] Several intermediates are reported in the degradations of anthracene, naphthalene, quinoline, and benzofuran, including several in which degradation leaves only one aromatic ring.[29,37,53] Pichat has also studied the degradation of pyridine and inferred a few of the larger intermediates in the degradation of pyridine from mass spectral patterns.[54]

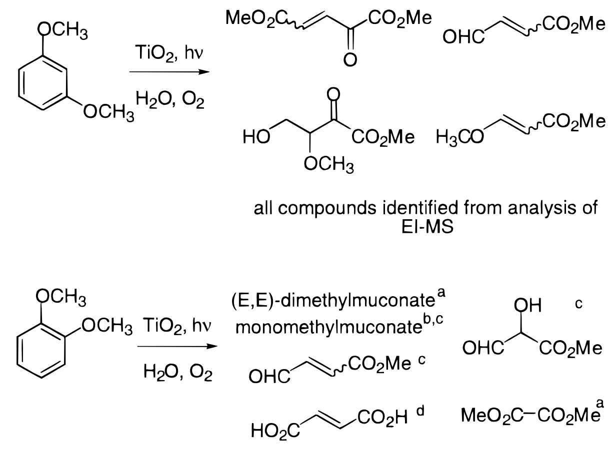

Figure 1. Intermediates in the photocatalytic degradation of dimethoxybenzenes.[33] (a) Identified by comparison to authetic sample. (b) Two isomers. (c) Identified by analysis of EI−MS of silylated derivative. (d) Identified by comparison to silylated derivative of authentic sample.

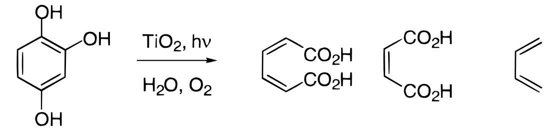

Figure 2. Intermediates detected by Olivé and co-workers by GC−MS from degradation of 1,2,4-benzenetriol.[41]

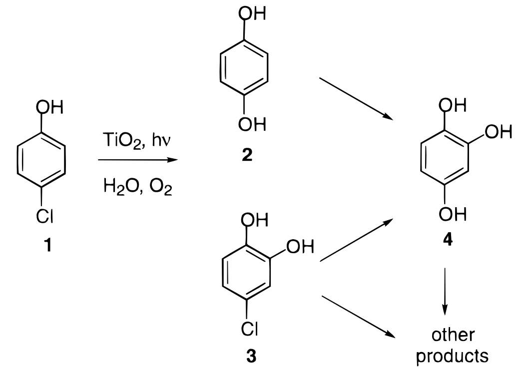

Figure 3. The first two oxidative steps in the degradation of 4-chlorophenol.

Previous reports have shown that there are two chemical transformations that compete as the first step in the photocatalytic degradation of 4-chlorophenol: substitution to form hydroquinone and hydroxylation to form 4-chlorocatechol (Figure 3). The precise conditions used and experimental setup determine the ratio of these two products.[5,6,12,15,19,21,24,46,47,49] Under our standard conditions (vide infra), about one-third of the chlorophenol is converted to hydroquinone; the remainder is hydroxylated. In this paper, we present a detailed analysis of the products obtained on partial photocatalytic degradation

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of hydroquinone. The identity of nearly every compound is confirmed by comparison to authentic samples.

Results

General Strategy And Techniques. Because the primary goal of this study was to identify as many intermediates as possible, degradations were carried out with relatively high concentrations of starting materials. Exploratory degradations were undertaken with the pH adjusted to several different values. It was found that the most intermediates were generally observed when the pH of the solution was approximately 8.5. Other than for the qualitative kinetics experiments described below, this pH was adopted as a standard for degradations.

To maximize concentrations of downstream intermediates, degradations were carried out using initial products. For instance, after examining the degradation of hydroquinone, a number of experiments were carried out using 1,2,4-benzenetriol **4** as starting material. Typical degradations were carried out with oxygen-saturated 100 mL aqueous samples containing 50 mg of TiO_2 (Degussa P-25). When analysis was done by HPLC, the initial concentration of the organic component was 1 mM. If GC or GC−MS was to be used, the initial concentration was 200 μM. Irradiations were carried out at ambient temperature using 8 4-watt "black light" lamps whose emission is broad and centered at 360 nm. The height of the solution nearly matched the length of the fluorescent tubes.

For kinetics experiments, solutions were buffered with phosphate and 1 mL samples were removed at various time points, filtered to remove the TiO_2, and analyzed by HPLC with a standard reverse phase column and diode array UV/Vis absorption detection.

For GC and GC−MS analysis, buffering was not practical. As a result, pH was maintained during photolysis within 0.5 pH units of the initial value by periodic addition of NaOH. Analysis carried out by using either organic extracts of the aqueous solutions or freeze-dried samples without further derivatization were unsuccessful. As a result, the degradation mixtures were silylated before analysis. Some degradation workups were additionally subjected to reduction with $NaBH_4$ or $NaBD_4$ before silylation.[55]

As controls to look for intermediates that strongly adsorbed to TiO_2,[56] partial degradations were carried out under conditions for GC analysis, except that instead of analyzing the filtrate, the residual TiO_2 was processed. In separate experiments, the TiO_2 was thoroughly washed with acidic, basic, and organic solvents and then subjected to the usual silylation conditions. Only trace quantities of degradation products were obtained, and it was concluded that they were inconsequential to the main experiments.

Degradation of Benzoquinone And Hydroquinone. Photocatalytic degradation is an oxidative process, and given the facile oxidation of hydroquinone to benzoquinone **5** under ordinary conditions, the result[57] that benzoquinone is rapidly reduced to hydroquinone by TiO_2 is somewhat counterintuitive. Because of the lack of dependence of this reaction on [O_2], it has been concluded that benzoquinone acts directly as an alternative electron sink.[57]

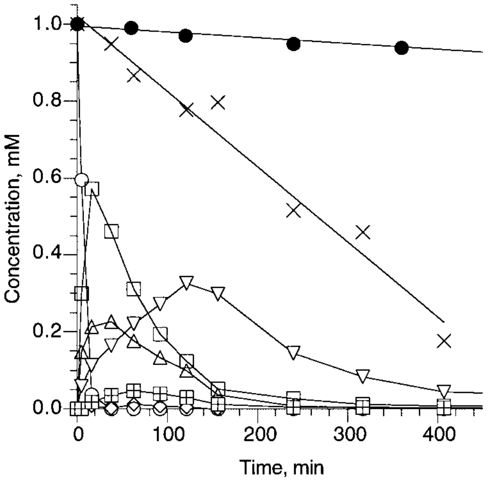
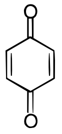


Figure 4. Degradation of 1 mM benzoquinone at pH 7 with 10 mM phosphate buffer. Benzoquinone, circles; hyrdoquinone, squares; hydroxybenzoquinone, triangles; 1,2,4-benzenetriol, diamonds; acyclic acids, inverted triangles; unidentified thermal product, crossed squares; scaled total organic carbon, ×; benzoquinone in dark control experiment, filled circles. The concentration of the acyclic acids is approximated by assuming the same extinction coefficient as that for hydroxybenzoquinone. The total organic carbon values are scaled to appear on the same axis as the identifiable compounds.

Degradations beginning with 1 mM benzoquinone, buffered to pH 7, were carried out and analyzed by HPLC. The disappearance profile of benzoquinone in the presence of TiO_2 and O_2 with and without light, shown in Figure 4, is consistent with literature reports on this point. With TiO_2 and light, benzoquinone is rapidly reduced to hydroquinone. A control photolysis carried out without TiO_2 showed less than 15% degradation in 20 h, so direct photolysis can be ignored. With TiO_2, intermediates with retention times of 1.99, 2.84, and 4.43 min were identified as hydroxybenzoquinone, 1,2,4-benzenetriol, and hydroquinone by comparison to authentic samples. A fairly broad peak with a retention time of 1.0 min contained the "last" intermediate of the degradation. Repetition of this experiment using GC analysis showed that a number of acyclic acids were present in the mixture. These compounds were unresolved by the HPLC separation, and it was concluded that the single HPLC peak represented the sum of all the acyclic products.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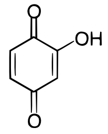

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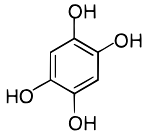

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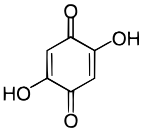

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Less than 1% of the original concentration of benzoquinone remained after 15 min, which also represented the approximate time of peak concentrations of hydroquinone and hydroxybenzoquinone (**6**). Hydroquinone is a clear primary product. Hydroxybenzoquinone is the major degradation product of hydroquinone (vide infra), but some formation of **6** directly from benzoquinone cannot be ruled out from this evidence. Finally, an

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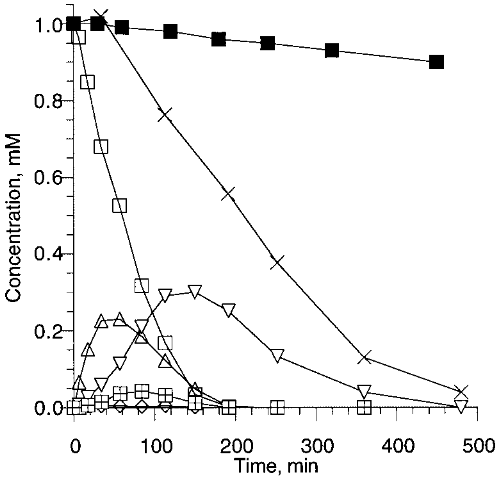


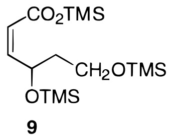
Figure 5. Degradation of 1 mM hydroquinone at pH 7 with 10 mM phosphate buffer. Hyrdoquinone, squares; hydroxybenzoquinone, triangles; 1,2,4-benzenetriol, diamonds; acyclic acids, inverted triangles; unidentified thermal product, crossed squares; scaled total organic carbon, ×; hydroquinone in dark control experiment, filled squares. The concentration of the acyclic acids is approximated by assuming the same extinction coefficient as that for hydroxybenzoquinone. The total organic carbon values are scaled to appear on the same axis as the identifiable compounds.

unidentified compound with a retention time of 1.33 min was observed. This compound appeared in the presence or absence of light and was attributed to the beginnings of oligomerization of benzoquinone.[58,59]

In the absence of TiO_2, hydroquinone is relatively stable at neutral pH. As expected, when the pH is higher, hydroquinone is air-oxidized to benzoquinone. With TiO_2 present but without light (i.e., the filled squares in Figure 5), hydroquinone is slowly decomposed, and the same unidentified dark product is produced as in the benzoquinone degradations.

Figure 5 shows the time profile of the photocatalytic degradation of hydroquinone obtained by HPLC. The apparent major primary product by HPLC analysis is hydroxybenzoquinone, accompanied by a small amount of 1,2,4-benzenetriol, but see below for discussion on this point. The acyclic acids are again recorded in a single HPLC peak that grows in secondarily.

GC−MS analysis was also carried out. The same compounds were observed in this case as described below for 1,2,4-benzenetriol degradations, but the important question was whether ring opening could be achieved directly from hydroquinone, as such products might easily be buried within the "diacid" HPLC peak. Indeed, a single, nearly negligibly small peak corresponding to direct cleavage of hydroquinone was observed when the workup included a reduction step. The observed peak was attributed to **9**, whose precursor is **10**.



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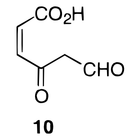

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Degradation of 1,2,4-Benzenetriol and Hydroxybenzoquinone. Compounds **4** and **6** have previously been observed as intermediates in degradations of 4-chlorophenol and other compounds. They enjoy the same redox relationship as hydroquinone and benzoquinone,[60] but unlike that pair, it is the quinone that was predominantly observed in our initial studies.

1,2,4-Benzenetriol is more quickly oxidized than hydroquinone in aqueous solution. In the presence of O_2, the oxidation is complete in a few minutes under basic conditions. Under neutral or acidic conditions, it is slower and incomplete. Moreover, **6** is not stable. In solutions of any pH, it slowly degraded to several other unidentified materials. In fact, we are unaware of any literature report of hydroxybenzoquinone as an isolated compound.

Analysis of **4** and **6** was not entirely satisfactory. HPLC analysis of anaerobically prepared solutions of the triol showed approximately equimolar quantities of triol and quinone, despite routine He-degassing of the HPLC solvents. This was attributed to oxidation during the analysis despite our at least modest precautions. If oxidation of **4** to **6** was carried to completion before HPLC analysis, only the quinone would be observed. In GC and GC−MS analysis, neither **6** nor its silylated derivatives were observed. It appears that **6** simply cannot withstand those conditions. HPLC traces thus overestimate the concentration of **6** at the expense of **4**, whereas GC analysis shows none of the quinone, whether or not it is actually found in the solution.

We were able to characterize **6** further by measuring its pK_a. A solution of **4** was made in air-saturated water at pH 8.5. Following complete oxidation, the sample was purged of O_2 with Ar, and UV spectra[60] were obtained as a function of pH. Isosbestic points were observed at 245, 280, 370, and 400 nm. The conjugate base had λ_{max} values at 261, 358 (broad shoulder), and 480 nm (very broad). A pK_a of 4.0 was obtained by measuring the UV intensity at 257 nm for the series of spectra.

Solutions of **4** (1 mM, pH 7.0, 10 mM phosphate buffer, 50 mg TiO_2 in 100 mL) were stable for 12 h in the dark in the absence of O_2. With the lights on but still in the absence of O_2, approximately 10% of the material degraded to other products in the same time period. In these control experiments, **4** is detected as a mixture with **6** as previously indicated. With O_2 present in otherwise identical solutions in the dark, **4** is converted to **6** in a few minutes, but **6** is completely converted to other materials, presumably humic precursors, over the course of several hours. The previously reported unknown dark product was part of this mixture. In all of these instances, the total organic carbon (TOC) remains unchanged.

With light, TiO_2, and oxygen available, **4** and **6** are degraded within 1 h. Degradations were carried out at pH 2.3, 4.5, 7.0, and 8.5. The TOC dropped to zero somewhat faster at the lower pH values. At pH 2.3, degradation was complete after 300 min, whereas about 20% of the TOC remained after 500 min at pH 8.5. Also, HPLC showed the largest buildup of the acyclic acids at this pH, reaching a maximum at approximately 40 min of photolysis.

Identification of Degradation Intermediates. Given the previous results, 1,2,4-benzenetriol was used as a starting material for these experiments, and a pH of 8.5 was adopted. To identify the compounds, GC−MS analy-

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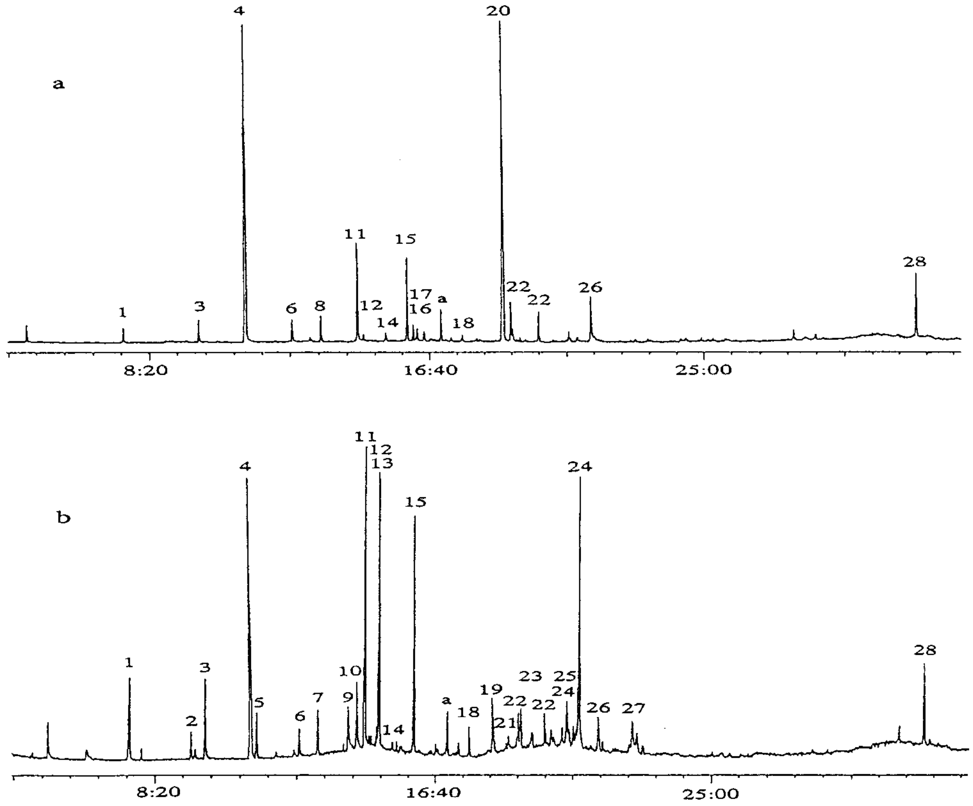
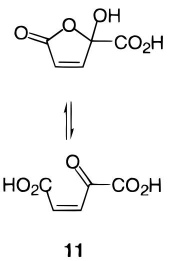


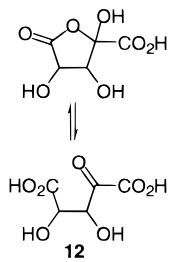
Figure 6. Representative GC traces obtained on partial photocatalytic degradation of 1,2,4-benzenetriol and silylation of the mixture. Traces were obtained (a) without and (b) with reduction of the mixture by $NaBH_4$ before silylation. The peak numbers refer to Table 1. The peak labeled "a" was not identified; see the Experimental Section.

sis was used, and the initial concentration of **4** was dropped to 200 μM. GC−MS analysis of the unfunctionalized degradation mixture was fruitless, no matter how it was processed, so the mixtures were silylated. Both alcohols and carboxylic acids were functionalized with TMS groups. To assist in the assignments and look for additional thermolabile compounds, the degradations were repeated, and the mixtures were reduced with $NaBH_4$ or $NaBD_4$ to convert ketones and aldehydes to alcohols before silylation. The combination of the three data sets was used to assign formulas for the unsilylated materials and make preliminary structural assignments. In most instances, these structural assignments were confirmed with samples of authentic material that was processed in the same way that showed the same chromatographic and MS behavior. Figure 6 shows a representative trace for both the nonreduced and reduced conditions. The data for the peaks in parts a and b of Figure 6 are given in Table 1. All of the numbered peaks except 16, 23, and 28 were identified with authentic compounds. Unlike a previous report,[41] neither butadiene nor muconic acid were detected in our mixtures. As can be seen in Table 1, several compounds (mainly aldehydes) were identified only when the reaction mixture was reduced. This was attributed to the parent compounds not surviving the GC conditions. Thus this list is representative and not exhaustive; even several very small observed peaks were not studied. Additionally, one peak was large enough to obtain a mass spectrum but was not identified.

Peak 26 in Table 1 was identified as 1,2,4,5-benzenetetraol, **7**. This clearly indicates that at least some fraction of the material is hydroxylated again before ring opening. Therefore new degradations were carried out using this material. Under the conditions used, **7** is rapidly oxidized to the quinone **8** in a dark reaction. Photocatalytic conditions apparently keep the reduced compound **7** available, on the basis of its appearance above. Degradations using HPLC detection showed only the aggregate acid peak observed previously. Degradations using GC−MS detection showed no other compounds with six carbons. The major compounds detected in those experiments were α-ketosuccinic acid (peak 18, Table 1), malonic acid (peak 15, Table 1), and oxalic acid (peak 4, Table 1).



11



12

The largest of the ring-opened intermediates that was readily available synthetically for further degradation studies was the five-carbon compound **11** (peak 19). Degradation of **11** yielded virtually the same group of smaller (four carbons and fewer) compounds as found in Table 1. The compound that is formed in highest concentration after modest degradation of **11** is **12** (peak 27). Other peaks, with small/medium/large notations, included 3*m*, 4*l*, 6*s*, 7*s*, 8*m*, 11*m*, 12*s*, 13*l*, 14*s*, 15*l*, 18*m*, 21*s*, 22*l*, and 25*s*. Partial degradations of maleic acid were also carried out. The peaks observed were 3*m*, 4*l*, 5*s*, 6*s*, 13*s*, 14*m*, 15*l*, 16*l*, 18*m*, and 22*l*.

Table 1. Products Resulting from the Photocatalytic Degradation of 1,2,4-Benzenetriol, Observed as TMS Derivatives by GC−MS

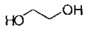
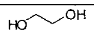
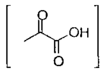
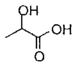
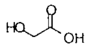
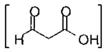
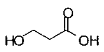
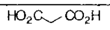
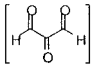
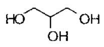
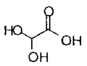
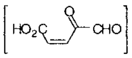
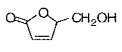
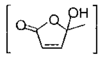
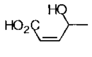
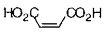
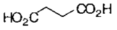
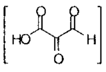
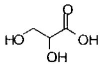
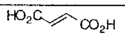
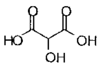
Peak No.	Intermediate	Reduced intermediate	R. T. Min.	F.W. CI	m/z values (relative abundance) EI
1			7.60	206	73(40), 147(100), 103(10), 191(30)
1	[OHC-CHO]		7.60	208	**NaBD$_4$**: 73(100), 103(10), 104(8), 147(40), 191(4), 193(5)
2			9.37	234	**NaBH$_4$**: 73(82), 117(23), 133(10), 147(100), 151(20), 174(10), 190(20), 191(38), 219(13) **NaBD$_4$**: 73(75), 111(18), 113(24), 117(13), 133(9), 147(100), 190(15), 192(30), 220(15)
3	Peak 8		9.69	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(4), 133(12), 147(100), 177(12), 178(6), 205(13), 206(6)
4	[HO_2C-CO_2H]		11.18	234	73(56), 133(4), 147(100), 190(23), 219(29)
5			11.26	234	**NaBH$_4$**: 73(64), 103(8), 117(8), 133(18), 147(100), 177(20), 219(16), 234(4) **NaBD$_4$**: 73(30), 104(12), 117(12), 118(6), 133(10), 147(100), 178(20), 220(24), 235(5)
6			12.55	248	73(29), 147(100), 233(16), 248(2)
7			13.12	308	**NaBH$_4$**: 73(90), 102(16), 103(10), 117(25), 133(25), 147(100), 205(45), 218(20), 248(8), 293(5) **NaBD$_4$**: 73(86), 103(8), 104(6), 133(15), 147(100), 207(8), 221(10), 296(4)
8			13.41	308	73(90), 147(100), 191(75), 219(20), 221(18), 265(3), 293(3), 308(4)
9			14.01	186	**NaBH$_4$**: 73(100), 103(35), 113(12), 143(10), 166(6), 171(10), 186(2) **NaBD$_4$**: 73(100), 104(40), 115(20), 145(22), 173(20), 188(4)
10			14.27	260	**NaBH$_4$**: 73(60), 133(12), 143(26), 147(100), 170(18), 217(5), 245(44), 260(12) **NaBD$_4$**: 73(56), 133(10), 143(12), 147(100), 172(5), 246(10), 261(2)
11			14.61	260	73(52), 75(10), 115(6), 133(7), 147(100), 170(16), 217(6), 245(18), 260(12)
12			14.66	262	73(35), 129(8), 147(100), 172(8), 247(28), 262(3)
13	 and Peak 16		14.93	322	**NaBH$_4$**: 73(100), 103(23), 117(18), 133(24), 147(75), 189(54), 205(20), 217(5), 292(34), 307(10) **NaBD$_4$**: 73(100), 103(18), 104(16), 133(35), 147(70), 190(45), 191(22), 293(36), 308(4), 309(12), 324(2)
14			15.30	260	73(16), 75(8), 143(22), 147(44), 245(100)
15			15.96	336	73(100), 102(30), 133(20), 147(80), 221(19), 292(32), 321(12)

Table 1 (Continued)

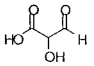
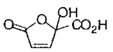
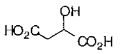
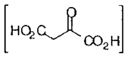
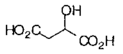
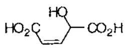
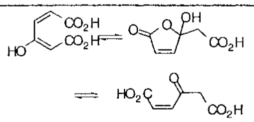
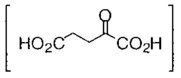
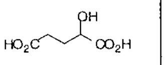
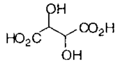
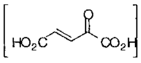
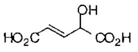
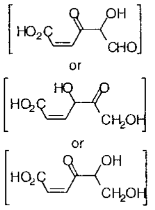
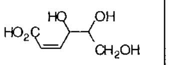
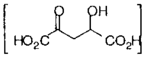
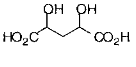
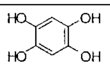
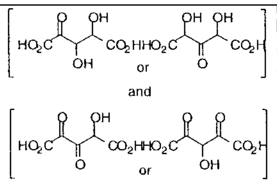
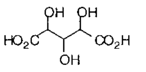
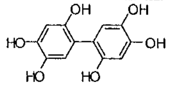
Peak No.	Intermediate	Reduced intermediate	R. T. Min.	F.W. CI	m/z values (relative abundance) EI
16			16.16	320	73(100), 133(10), 143(15), 147(65), 221(35), 305(10), 320(2)
17			16.25	288	73(100), 133(15), 147(90), 171(15), 173(13), 201(10), 243(8), 273(10), 288(8)
18			17.65	350	73(100), 101(12), 133(20), 147(80), 175(11), 265(10), 307(7), 335(16)
18			17.65	351	**NaBD$_4$**: 73(100), 102(15), 117(10), 133(10), 147(40), 264(5), 266(7), 308(5), 334(10), 336(8)
19	Peak 17		18.23	362	**NaBH$_4$**: 73(100), 112(4), 133(8), 147(22), 156(10), 217(5), 245(5), 318(12), 347(4) **NaBD$_4$**: 73(100), 113(4), 133(8), 147(30), 157(16), 218(6), 246(4), 319(4), 348(6)
20			18.83	374	73(54), 133(8), 147(28), 257(100), 330(18), 359(14)
21			18.85	364	**NaBH$_4$**: 73(100), 129(70), 147(86), 157(18), 203(20), 247(56), 259(15), 275(6), 349(20) **NaBD$_4$**:73(92), 130(100), 147(60), 158(14), 204(40), 248(70), 350(30)
22			19.05 19.90	438	73(100), 133(15), 147(76), 189(20), 219(40), 221(11), 292(66), 305(14), 333(8), 423(18)
23			19.50	362	**NaBH$_4$**: 73(100), 133(8), 147(45), 156(25), 187(4), 217(8), 245(10), 272(2), 303(2), 347(2) **NaBD$_4$**: 73(100), 133(14), 147(50), 157(20), 188(5), 218(6), 232(10), 246(10), 319(18), 348(10)
24			20.62 21.12	450	**NaBH$_4$**: 73(100), 129(15), 133(12), 147(35), 191(12), 217(16), 218(22), 243(20), 255(6), 271(4), 305(10), 333(8), 345(8), 435(15), 450(3) **NaBD$_4$**: 73(100), 130(18), 133(18), 147(68), 192(12), 218(16), 219(35), 244(18), 245(24), 306(7), 335(8), 347(6), 437(20), 452(5)
25			20.91	452	**NaBH$_4$**: 73(100), 129(8), 133(16), 147(92), 204(10), 217(12), 219(8), 233(8), 245(82), 292(10), 319(12), 335(10), 437(5) **NaBD$_4$**: 73(100), 129(4), 133(14), 147(68), 205(4), 218(8), 219(12), 246(35), 293(15), 320(20), 336(12), 438(14)
26			21.60	430	73(100), 133(20), 147(60), 179(40), 193(20), 207(10), 254(10), 267(5), 327(10), 415(22), 430(15)
27			22.15 22.29 22.42	540	**NaBH$_4$**: 73(100), 131(5), 133(3), 143(8), 147(20), 292(40), 333(10), 407(5), 525(8) **NaBD$_4$**: 73(100), 133(8), 144(3), 147(52), 190(10), 221(10), 278(10), 292(40), 293(38), 294(30), 321(10), 322(10)), 334(8), 408(10), 436(3), 437(5), 526(8), 527(7)

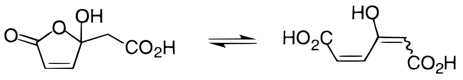
Table 1 (Continued)

Peak No.	Intermediate	Reduced intermediate	R. T. Min.	F.W. CI	m/z values (relative abundance) EI
28			31.52	682	73(100), 133(10), 147(47), 207(8), 269(5), 341(14), 341(10), 594(5), 667(9), 682(10)

Photoreaction condition: [1,2,4-benzenetriol]$_0$ = 200 μM, pH 8.5, Vol. = 100 ml, TiO_2 = 50 mg, t = 20 min, T = 25 °C.

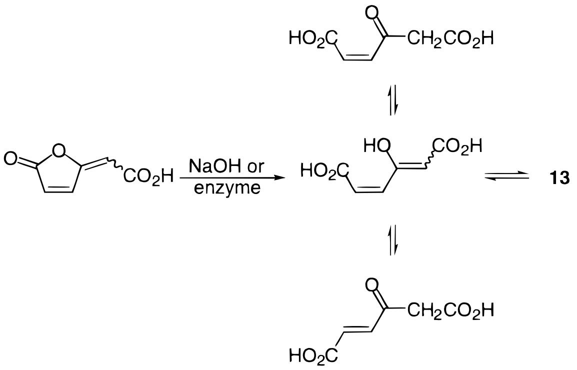
Compounds in brackets were not observed without reduction. Retention times given in the format of Min.Sec.

Preparation of Authentic Samples. The preparations of a number of the authentic samples was accomplished and are reported in the Experimental Section. There was one important compound of which we were unable to prepare a pure sample but in whose assignment we are confident nonetheless. This compound, containing six carbons and corresponding to peak 20, merits discussion.

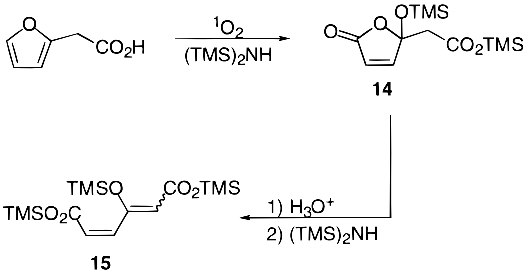


13

The compound giving rise to peak 20 contains three TMS groups, as determined from its molecular weight. The compound must have at least three oxygen atoms and no more than six carbons. The underivatized compound must have a molecular weight of 158. There is not a reasonable five-carbon molecule with that formula; thus the underivatized formula is $C_6H_6O_5$. Compound **13** (and its various tautomers) was chosen as a candidate molecule with this formula.



(*Z*)-4-Oxohex-2-enedioic acid, the open, ketonic form of **13**, has not been isolated but is generated in situ as a mixture with the *E* compound and enol from a dienelactone in the biodegradation literature.[61] An alternative preparation was sought that might yield a pure sample of the Z tautomers. After several other attempted routes, furanacetic acid was oxidized with singlet oxygen in pyridine containing vanadium pentoxide and excess hexamethyldisilazane. These conditions were used to minimize tautomerization before trapping. A mixture of several compounds resulted. The major compound, approximately half of the mixture, was assigned by NMR to be the di-TMS derivative of **13**, i.e., compound **14**. Controlled hydrolysis of this mixture at pH 3, followed by standard silylating conditions, resulted in a new mixture that contained a substantial quantity of **15**. The GC−MS of this mixture contained a substantial amount of peak 20 of Table 1, thus assigned to be **15**.



The structure of **15** was obtained by ^{1}H and ^{13}C NMR spectroscopy and by comparison of the MS spectrum to that previously obtained by the literature method of in situ synthesis of **13/15**.[62] Moreover, the MS was essentially identical to that of the TMS derivative of (*E*)-4-oxohex-2-enedioic acid, which was independently prepared,[63] even though the two had different GC retention times.

The assignment was confirmed by a second independent synthesis. A cleaner preparation was achieved by treatment of 1,2,4-benzenetriol with peracetic acid in acetic acid, catalyzed with $Fe(OAc)_3$. This resulted in a mixture that was approximately 60% **13**, 20% the *trans* (uncyclized) isomer, a few minor unidentified compounds, and some residual acetic acid. Silylation of the mixture under standard conditions and GC analysis resulted in confirmation that peak 20 was indeed **15**.

Discussion

This paper presents, to the best of our knowledge, the most extensive collection of intermediates in the photocatalytic degradation of organic compounds to date, though even this is not complete. In fact, no aldehydes were detected without reductive workup. Control experiments with undegraded glutaraldehyde were consistent with that observation. Nonetheless, the extensive lists of stable intermediates must be taken as at least very representative of the mixture of organic compounds obtained in partial degradations

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[61] Kaschabek, S. R.; Reineke, W. *J. Bacteriol.* **1995**, *177*, 320−325.

[62] Rieble, S.; Joshi, D. K.; Gold, M. H. *J. Bacteriol.* **1994**, *176*, 4838−4844.

[63] Kaeata, M.; Mizutani, Y.; Shinriki, M.; Kimura, M.; Ishidate, M. *Chem. Pharm. Bull.* **1970**, *18*, 50−54.

On irradiation with UV light, charge separation occurs in the TiO_2 particles. A cascade of reactions is set off:[5,64−66]

$$TiO_2 \xrightarrow{h\nu} h^+_{VB} + e^-_{CB} \tag{1}$$

$$H_2O_{ads} + h^+_{VB} \rightarrow {}^\bullet OH_{ads} + H^+ \tag{2}$$

$$O_2 + e^-_{CB} \rightarrow O_2^{-\bullet} \tag{3}$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet \tag{4}$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{5}$$

$$H_2O_2 + e^-_{CB} \rightarrow {}^\bullet OH + HO^- \tag{6}$$

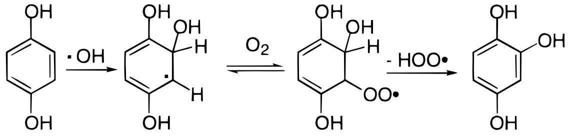
$$A + e^-_{CB} \rightarrow A^{-\bullet} \tag{7}$$

$$D + h^+_{VB} \rightarrow D^{+\bullet} \tag{8}$$

Here A and D are potential surface-bound organic electron donors and acceptors, and it is also assumed that a certain small fraction of the adsorbed hydroxyl radicals diffuse into bulk solution. Though there is some debate on the exact nature of the hydroxyl species, we take a surface-bound $HO^\bullet$ to be a reasonable description.[67,68] The subsequent reactions of surface-bound and diffusing hydroxyl radicals are the initiating microscopic steps for most degradation reactions of organic substrates in aqueous solution. Some reactions may also initiated by direct hole oxidation when the substrate is bound to the TiO_2. It is assumed that many initially formed organic radicals react with O_2, though reaction with superoxide or hydroperoxyl is plausible for materials oxidized in the viscinity of a TiO_2 particle because of the high local concentration of the oxygen species. Hydrogen peroxide and hydroperoxyl radicals serve as hydrogen atom donors, and loss of hydroperoxyl is assumed to be a reasonable microscopic step to form closed shell species.

In the following paragraphs, we use these basic steps to suggest pathways for the formation of many of the observed compounds. We borrow liberally from the pulse radiolysis and atmospheric oxidation literature (see, for instance, references 26 and 69−74) but also note that the conditions of radiolysis and other hydroxyl-radical-generating systems such as Fenton chemistry can generate much different results.[13,15,75,76] We have not written mechanisms involving the combination of peroxyl radicals to give tetroxides, on the assumption that steady-state concentrations of the peroxyls are low. However, most of their typical reactions are modeled reasonably well on the assumption of similar superoxide/hydroperoxide chemistry. Nonetheless, these substances may be formed to a minor extent, and their decomposition may contribute to the formation of some products.

In the degradation of hydroquinone, the results of Richard[57] and now ourselves clearly seem to show that benzoquinone is not an important player, as it is quickly reduced even if formed. Benzenetriol **4** is produced by hydroxylation. Oxygenations of this sort are generally presumed to occur by addition of $HO^\bullet$, followed by reaction with O_2 and elimination of $HOO^\bullet$, as shown in eq 11.



4

(11)

Only a tiny fraction of hydroquinone undergoes ring opening; hydroxylation is by far the major pathway. The mechanism proposed below for cleavage of **4** leads to **10** when hydroquinone is instead its substrate. The mechanism is also entirely consistent with **4** being a better substrate.

The predominance of 1,2,4 benzenetriol over hydroxybenzoquinone under the degradative conditions is not as clearly demonstrated by these experiments as for hydroquinone over benzoquinone because of the ease of dark air-oxidation of the triol, which affects the HPLC analysis. It has been assumed for purposes of this discussion that, like hydroquinone/benzoquinone, the triol is the major actor. One reason to have confidence in this suggestion is that 4-chlorocatechol undergoes analogous cleavage between the two hydroxyl groups.[77]

In contrast to hydroquinone, in which hyroxylation is the major reaction, for **4** hydroxylation is significantly less important that C−C bond cleavage. We propose that the reason for this that the major mechanism of reaction changes from $HO^\bullet$ addition to single electron oxidation. Two six-carbon peaks in which the aromatic ring has been cleaved are observed, peaks 20 and 24. The larger of these is peak 20, which was identified as the silylated derivative of **13**. Although the structure that leads to peak 24 was not uniquely determined, we believe it most likely to be aldehyde-acid **20** shown as one of the possible precursors in Table 1. The reason for this becomes clear as the cleavage mechanism is considered.

It is proposed that the cleavage reaction comes about as shown in Figure 7. The figure is drawn without regard to the mode of binding of the substrate to TiO_2 or to protonation state. Neither is expected to have a gross

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(64) Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341−357.

(65) Serpone, N. *Res. Chem. Int.* **1994**, *20*, 953−992.

(66) Fox, M. A. *The Role of Hydroxyl Radicals in the Photocatalyzed Detoxification of Organic Pollutants: Pulse Radiolysis and Time-Resolved Diffuse Reflectance Measurements.* In *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier: New York, 1993; Vol. 3, pp 163−167.

(67) Goldstein, S.; Czapski, G.; Rabani, J. *J. Phys. Chem.* **1994**, *98*, 6586−6591.

(68) Serpone, N.; Pelizzetti; Hidaka, H. Identifying primary events and the nature of intermediates formed during the photocatalyzed oxidation of organics mediated by irradiated semiconductors. In *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier: New York,1993; Vol. 3, pp 225−250.

(69) von Sonntag, C.; Schuchmann, H.-P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1229−1253.

(70) Pan, X.-M.; Schuchmann, M. N.; von Sonntag, C. *J. Chem. Soc., Perkin Trans. 2* **1993**, 289−297.

(71) Lay, T. H.; Bozzelli, J. W.; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 6543−6554.

(72) Andino, J. M.; Smith, J. N.; Flagan, R. C.; Goddard, W. A., III; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 10967−10980.

(73) Ulanski, P.; Bothe, E.; Rosiak, J. M.; von Sonntag, C. *J. Chem. Soc., Perkin Trans. 2* **1996**, 5−12.

(74) Leitner, N. K. V.; Dore, M. *J. Photochem. Photobiol., A* **1996**, *99*, 137−143.

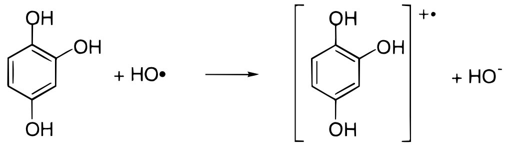
(75) Spacek, W.; Bauer, R.; Heisler, G. *Chemosphere* **1995**, *30*, 477−484.

(76) Legrini, O.; Oliveros, E.; Braun, A. M. *Chem. Rev.* **1993**, *93*, 671−698.

(77) Li, X.; Cubbage, J. W.; Jenks, W. S. *J. Org. Chem.* **1999**, *64*, 8525−8536.

effect on the mechanism, save for the availability of h^+_{VB} as an electron-transfer agent.

It is well known that *o*-hydroquinone derivatives adsorb to the TiO_2 much more strongly than do chlorophenol, *p*-hydroquinone, etc.[78–83] This would give rise to a higher likelihood of direct oxidation. Indeed, Kesselman et al. provide strong evidence that 4-chlorocatechol is adsorbed and electrochemically oxidized in a modified TiO_2 electrode, whereas hydroxyl radical reactions are more important for the poorly adsorbing 4-chlorophenol.[81,82] Hole oxidation has been implicated in several systems, generally when adsorption is strong. (See, for instance, references 15,30,34,37,53,67,84,85.) Further, with a trioxygenated benzene, it becomes more plausible for the hydroxyl radical or its surface-bound equivalent to react by electron transfer as shown in eq 12. It is difficult with only the current evidence to distinguish between h^+_{VB} and $^\bullet OH_{ads}$, but the difference may be semantic, because these are often viewed as synonymous species.



(12)

A similar net one-electron oxidation can be achieved by addition of $HO^\bullet$, followed by elimination of water. This has the net result of hydrogen abstraction of a phenolic hydrogen atom. (In fact, it is quite likely that $\mathbf{4}^{\bullet+}$, formed by single electron transfer, would spontaneously deprotonate in slightly basic water, giving exactly the same compound.) Like the chemistry in Figure 7, superoxide could subsequently react and cleave a carbon–carbon bond. However, it is not clear why this mechanism would be favored for **4** but not hydroquinone, so we favor simple electron transfer.

Compound **13** (i.e., peak 20) clearly derives from cleavage of the C_1-C_2 bond of **4**. If the source of the oxygen atoms was $HO^\bullet$ rather than O_2, $HO^\bullet$ attack would have to occur at either of these two positions to account for this cleavage. However, $HO^\bullet$ is interpreted as an electrophilic reagent, and the *ipso* carbons of **4** are not the nucleophilic positions; carbon 3 is the most so as judged by calculated electrostatic potentials (Table 2). The calculations presented in Table 2 were done with a dielectric continuum model for water rather than any specific binding mode for TiO_2, but this is not expected to qualitatively change the results as they relate to this point. Indeed, the only observed hydroxylation product of **4** is **7**, in which $HO^\bullet$ has apparently reacted at precisely the carbon with the most negative electrostatic potential.

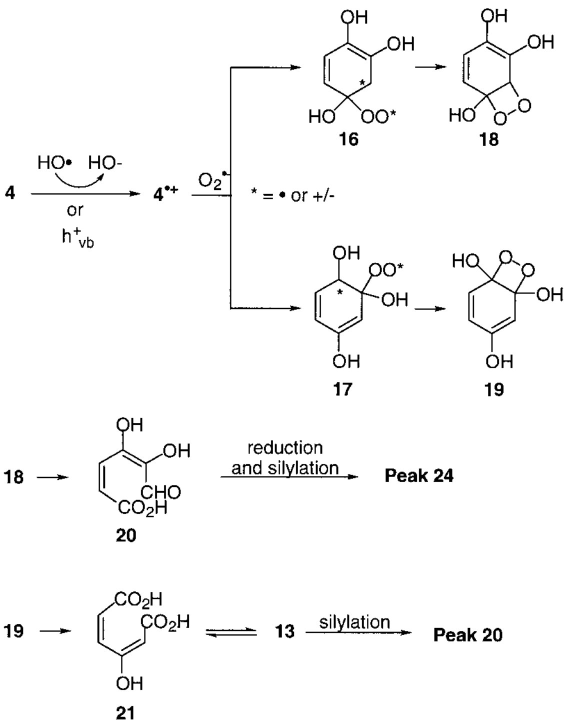
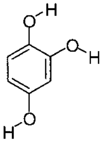
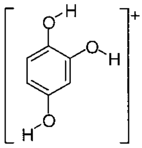
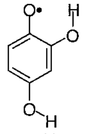
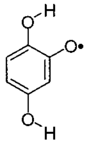
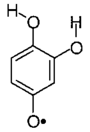


Figure 7. Proposed one-electon oxidation mechanism for carbon–carbon bond cleavage to open rings.

Table 2. Calculated Electrostatic Potentials at Each Carbon for Compounds Related to 4[a]

Compound	C1	C2	C3	C4	C5	C6
	0.14	0.52	-0.65	0.50	-0.37	-0.26
	0.36	0.61	-0.70	0.65	-0.20	-0.30
	0.44	0.42	-0.66	0.60	-0.31	-0.29
	0.30	0.64	-0.78	0.62	-0.30	-0.26
	0.28	0.55	-0.69	0.77	-0.36	-0.24

[a] All compounds were fully optimized at RHF/6-31G(d) or ROHF/6-31G(d) as appropriate. They are drawn in the approximate conformation. Calculations include a dielectric continuum model to take water solvent into account.

Granted that the radical cation $\mathbf{4}^{\bullet+}$ is formed, the regiochemistry of cleavage implicates superoxide, which predominates over $HOO^\bullet$ at the pH used here, as the agent that traps the organic radical cation. Trapping of $\mathbf{4}^{\bullet+}$ occurs at the two carbons of highest electrostatic

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(78) Cunningham, J.; Sedlak, P. *J. Photochem. Photobiol., A* **1994**, *77*, 255–63.

(79) Mills, A.; Morris, S. *J. Photochem. Photobiol., A* **1993**, *71*, 75–83.

(80) Tunesi, S.; Anderson, M. *J. Phys. Chem.* **1991**, *95*, 3399–3405.

(81) Kesselman, J. M.; Lewis, N. S.; Hoffmann, M. R. *Environ. Sci. Technol.* **1997**, *31*, 2298–2302.

(82) Kesselman, J. M.; Weres, O.; Lewis, N. S.; Hoffmann, M. R. *J. Phys. Chem. B* **1997**, *101*, 2637–2643.

(83) Vasudevan, D.; Stone, A. T. *Environ. Sci. Technol.* **1996**, *30*, 1604–1613.

(84) Sun, Y.; Pignatello, J. J. *Environ. Sci. Technol.* **1995**, *29*, 2065–2072.

(85) Tahiri, H.; Ait Ichou, Y.; Herrmann, J.-M. *J. Photochem. Photobiol., A* **1998**, *114*, 219–226.

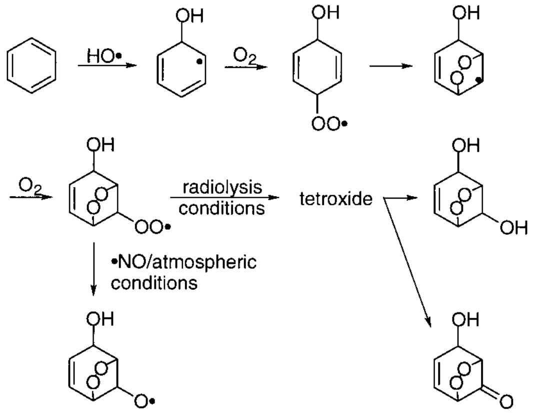


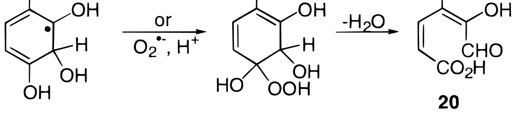
Figure 8. Representative pathways of benzene oxidation under radiolysis and atmospheric conditions.

potential (regardless of deprotonation, Table 2). Intermediates **16** and **17** are quite likely to be of zwitterionic character, particularly in water. This would seem to guide the regiochemistry of dioxetane closure as shown. Collapse gives dioxetanes **18** and **19**, which in turn trivially decompose to the acid-aldehyde **20** or the diacid **21**. After workup for GC analysis, these yield peaks 24 and 20, respectively.

In proposing this mechanism, the involvement of superoxide is simply postulated to account for the regiochemistry. Its ability to predominate over neutral O_2 trapping in photocatalytic reactions has been suggested before, and some specific evidence involving use of superoxide dismutase (SOD) has supported this idea.[29,31,33,53]

Only one closure regiochemistry of the intermediates **16** and **17** is illustrated. Closure of **16** with the other possible regiochemistries, followed by rupture of the dioxetane or endoperoxide also looks reasonable on paper. There is no evidence of the products derived from the dioxetane isomers not shown in Figure 7, but 1−4 closure of **16**, followed by fragmentation of the endoperoxide could lead to peaks 11 and 18. For **17**, the alternate closures and fragmentations do not lead to observed products.

Reaction of **4** with electrophilic hydroxyl radical by addition would be expected to occur at the carbons without oxygen substitution, mostly at carbons 3 and 5. The latter leads to **7**. Addition of $HO^{\bullet}$ at carbon 3 can lead to an alternate mechanism for formation of **20**, as shown in eq 13. However, it seems more likely that reaction of the hydroxyl adduct with O_2 or $O_2^{-\bullet}$ would lead to a dienone, and we favor the one-electron oxidation mechanism.

 (13)

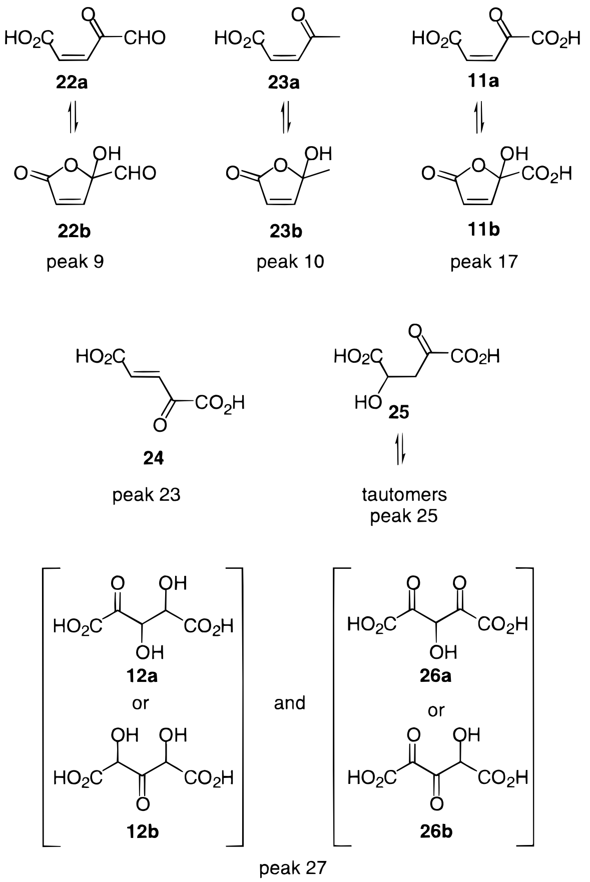


Figure 9. The observed five-carbon derivatives of 1,2,4-benzenetriol.

In the literature concerning atmospheric oxidation or aerated pulse radiolysis of benzene or phenol, chemistry similar to this is involved, and one such course is illustrated in Figure 8. Addition of $HO^{\bullet}$ and then O_2 is generally assumed. In addition to loss of $HOO^{\bullet}$, it is often proposed that cyclization to an endoperoxide-containing radical occurs. This is followed by addition of another molecule of O_2. In the radiolysis work, formation of a tetroxide is assumed. Its decomposition leads to an alcohol and ketone, each of which can readily fragment into acyclic products.[70] In the atmospheric chemistry, an O atom is thought to be removed by $^{\bullet}NO$, leaving an alkoxyl radical that can fragment into two- and four-carbon pieces.[71,72] Although superficially attractive here, the change in chemistry invoked by having three extant hydroxyls on the ring makes this pathway appear problematic. Because of the observation of **7**, we know that some HO addition occurs at carbon 5 of **4**. The products that would be formed by straightforward application of the endoperoxide/tetroxide pathway of Figure 8 are not observed, regardless of whether initial hydroxyl addition occurs at carbon 3, 5, or 6. Additionally, it is not unreasonable to derive the “atmospheric type” alkoxyl radical analogue from the peroxyl under the present conditions where $HOO^{\bullet}$ (or its net atoms) are available. However, the further degradation product would always be a four-carbon aldehyde, none of which are observed.

We turn now to the five-carbon peaks (Figure 9). All of them, save **25** and peak 27, have two consecutive sp^2 carbons that are otherwise unoxidized. This is in common with both **20** and **21**; it is thus reasonable to presume that they may be derivatives of one or both of these compounds in the absence of paths leading directly from **4**. Oxidation of **13** by direct reaction of h^{+}_{VB} or $HO^{\bullet}$ followed by decarboxylation yields **27** (Figure 10) by the photo-Kolbe reaction. In turn, this radical can be converted to the hydroperoxide **28** by a variety of paths involving either reaction with O_2 or $O_2^{-\bullet}$. Dehydration leads to **22**. Oxidation of aldehydes to acids is expected

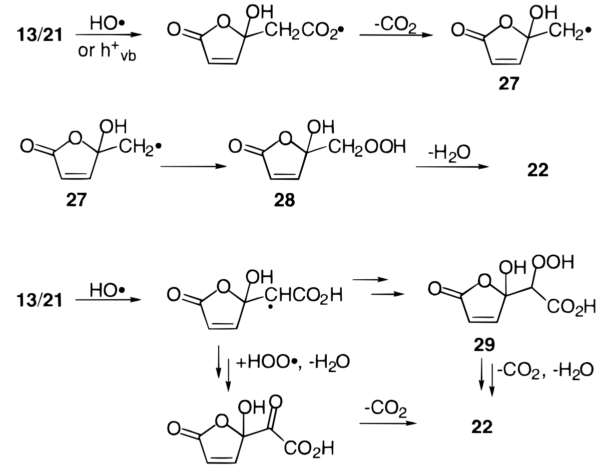


Figure 10. Possible mechanisms for formation of **22**.

to be facile under these conditions, either by a second hydrogen abstraction from either the aldehyde or its hydrated analogue or by Baeyer-Villager-type chemistry of a peroxide. Such chemistry leads to compound **11**. The photo-Kolbe reaction has been observed previously for both aromatic and aliphatic acids under similar conditions[84-87] but does not often dominate the chemistry.[74,88,89] An alternative would be hydrogen abstraction at the saturated carbon. As illustrated, this also leads to **22** by more than one plausible path. Similar oxidative pathways can be written starting from **20** rather than **21**.

Compound **23** is clearly the decarboxylation product of **13/21**. It is, in fact, plausible that **13/21** is converted entirely to **23**, from which the other compounds in this channel are derived. This cannot be determined without further data.

The appearance of **24** is of little surprise. During various unreported synthetic attempts, E/Z isomerization of this and related systems was a major difficulty. Compound **25** is the hydration product of **11**. The mechanism of the hydration is not known, but the same reaction is also observed in degradations of maleic acid.

The compounds given as **12** and **26** are pairs of tautomers. At least one of each pair is necessary to explain the deuterium incorporation observed in Table 1. Because they are so highly oxidized, it is difficult to attribute exact pathways. It is convenient to speculate that **12a** derives from dihydroxylation of **11**. Peak 27 is one of the largest observed in degradations that were carried out starting only with **11**. We also note that a similar dihydroxylation product (tartaric acid) is the major oxidized product in partial degradations of maleic acid.

It is not as straightforward to write an $HO^{\bullet}$-based mechanism for dihydroxylation of an olefin using only the chemistry invoked so far. Tetroxides present a plausible solution. Another solution involves two chemical steps: conversion of the olefin to a ketone and then hydration of the olefin, for instance. A further alternative exists. Fox and co-workers have investigated and reviewed the preparative synthetically useful chemistry of TiO_2 photolysis in anhydrous solutions of various organic molecules.[90,91] One of those reactions is the oxidative cleavage of olefins to two carbonyl compounds in organic solvents in the presence of O_2. Depending on conditions, yields of up to 30% of the *epoxide* were also obtained.[91] Spectroscopic evidence showed that the reaction was very likely initiated by one-electron oxidation of the substrate,[92] but a detailed mechanism for epoxide formation was not obtained. The epoxide is at the same oxidation state as the diol, so it is plausible that the diols observed here are simply the hydration product of this same reaction.

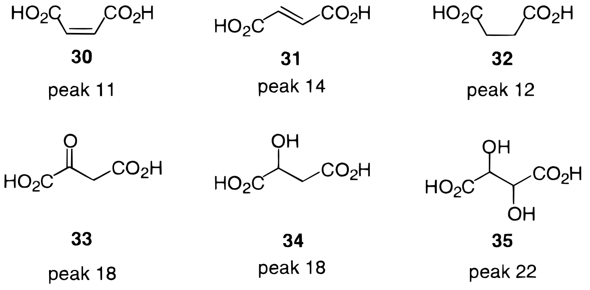
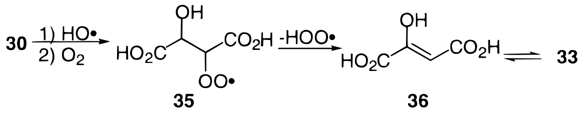


Figure 11. Four-carbon compounds observed on degradation of 1,2,4-benzenetriol.

The four-carbon compounds are shown in Figure 11. Maleic acid (**30**) is the most prominent four-carbon compound in the degradations of **4**, and it is straightforward to write pathways to it via **11** and/or **22**. Fumaric acid derives either from E/Z isomerization of maleic acid or from degradation of something that has undergone the isomerization earlier. Succinic acid was not observed during our partial degradation of **30**, but it is only a small peak in degradation of **4**. α-Ketosuccinic acid is one of the important peaks in the degradation of **11** and **30**. A reasonable route from maleic acid is shown below, in which the β-hydroxyperoxyl radical eliminates $HOO^{\bullet}$. Elimination of $HOO^{\bullet}$ to form either carbonyls or aromatic rings is spontaneous and rapid under pulse radiolysis conditions,[69] but elimination to form unconjugated enols in carboydrates is not observed by transient techniques in the absence of base catalysis.[93] However, the relatively high pH used here and the extended conjugation of **36** appear to justify the proposal.



As in the five-carbon set, the appearance of **34** is suggestive of hydration of the olefin. As indicated in Table 1, **33** was not implied by the analyses unless the sample was reduced to give **34** before silylation. Reduction with $NaBD_4$ allows one to determine that the precursors to the peak are both **33** and **34**. The relative intensities of the peaks for the deuterated and undeuterated com-

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(86) Sakata, T.; Kawai, T.; Hashimoto, K. *J. Phys. Chem.* **1984**, *88*, 2344–2350.

(87) Dixon, W. T.; Norman, R. O. C.; Buley, A. L. *J. Chem. Soc.* **1964**, 3625–3634.

(88) Matthews, R. W. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 457–571.

(89) Chemseddine, A.; Boehm, H. P. *J. Mol. Catal.* **1990**, *60*, 295–311.

(90) Fox, M. A. *Top. Curr. Chem.* **1987**, *142*, 72–99.

(91) Fox, M. A. Mechanistic Photocatalysis in Organic Synthesis. In *Photocatalysis: Fundamentals and Applications*; Serpone, N., Pellizzetti, E., Eds.; John Wiley & Sons: New York, 1989; pp 421–455.

(92) Fox, M. A.; Lindig, B. L.; Chen, C.-C. *J. Am. Chem. Soc.* **1982**, *104*, 5828–5829.

(93) Bothe, E.; Schulte-Frohlinde, D.; von Sonntag, C. *J. Chem. Soc., Perkins Trans. 2* **1978**, 416–420.

pounds indicate that both compounds contribute comparably to the total peak found from the degradation of **4**. Similarly, degradation of maleic acid shows peak 18 when the reaction was not reduced before silylating. As a result, it can be concluded that similar quantities of both **33** and **34** are produced and that maleic acid is at least one of their precursors.

The discussion to this point makes it abundantly clear that the farther away a degradation product is from the material from which the degradation began, the less tenable are statements about the degradation product's direct origins. In this spirit, we will refrain from commenting further on pathways that might lead to the two- and three-carbon compounds in Table 1 and leave this to a subsequent investigation.

Relationship of Current to Previous Work. As alluded to previously, there have been relatively few reports on the intermediate products of photocatalytic degradation of aromatic compounds beyond the first step or two of hydroxylations. Olivé and co-workers did briefly report on the degradation of **4**, giving maleic acid, muconic acid, and butadiene as the major products.[41] Of these, we observed only maleic acid, but as mentioned previously, it is likely that butadiene would have eluded our detection method. However, it must be pointed out that both muconic acid and butadiene contain four consecutive non-oxygenated carbon atoms, thereby requiring at the very least a reduction and dehydration to be formed from **4**.

The work of Pichat on *o*-dimethoxybenzene[33] is more in line with our results. They reported the observation of isomers of mono- and dimethyl muconate. No other six-carbon ring-opened compounds were reported, notably none that were hydroxylated. Although the lack of hydroxylated products is surprising, the muconates themselves are consistent with the cleavage of **4** to give **21**. Moreover, their subsequent work with SOD in this system[94] and others is consistent with superoxide as a key reagent in the cleavage step. We believe this is very supportive of the cleavage mechanism presented in Figure 7.

Similarly, Pichat's degradation of quinoline demonstrates by regiochemical arguments similar to those presented here that oxidation can occur by hole oxidation and nucleophilic trapping by superoxide.[29] Oxidation of quinoline by $HO^\bullet$ (photo-Fenton) occurs on the more electron-rich benzene ring, whereas oxidation with TiO_2 occurs substantially on the pyridine moiety. Trapping of the radical cation occurs on the comparatively electron-poor portion of the ring system, consistent with a nucleophilic reagent such as superoxide. Cleavage in the quinoline case is thought to yield aldehydes rather than acids. This is consistent with the present discussion, as long as the thermodynamically reasonable single electron oxidation of quinoline occurs. The ratio of products apparently due to $HO^\bullet$ oxidation versus $h^+/O_2^{-\bullet}$ change in a predictable way with variations in pH and addition of SOD.

Theurich et al. report the degradation of naphthalene and anthracene with TiO_2 at low pH.[37] For naphthalene, naphthoquinone and the epoxide of naphthoquinone were the main noncleaved intermediates, though *o*-naphthoquinone and other materials were observed. The major cleaved intermediate was 2′-formyl-(*Z*)-cinnamaldehyde, but both of the corresponding acid-aldehydes are also observed. Though they suggest that *o*-naphthoquinone is the immediate precursor to 2-formyl-(*Z*)-cinnamaldehyde, no particular mechanism is suggested. In light of the current work and the quinoline degradation, it may be suggested that the cleavage may not proceed through the *o*-quinone at all but may be accounted for using a scheme like Figure 7 in which naphthalene is directly oxidized.

Pichat's group has also examined the degradation of pyridine.[54] The major cleavage products, identified by analysis of the GC−MS data, are all dialdehydes. It was suggested that these aldehydes derive from unobserved *o*-bis-hydroxylated materials, but no explanation as to from where the aldehydic protons are derived is given. Again, it would be consistent with the present data and with the quinoline work to think that perhaps the ring-opening reactions occurs as in Figure 7 from pyridine and pyridone.

Of all of the systems investigated, the quinoline and current data are best documented. The clever use of quinoline with its variation of electron demand to probe the electron demand of different reagents clearly demonstrates a mechanism exists beyond $HO^\bullet$ radical addition, and the SOD and pH experiments support the one-electron oxidation and capture by superoxide. In the present case, distinct differences in electron demand exist within the same ring for 1,2,4-benzenetriol. There exists some ambiguity for the cleavage products that make up peak 24, but there is no doubt that **21** (and its tautomers) is the main cleavage product. The known proclivity of $HO^\bullet$ for electron-rich positions of aromatic systems makes a strong argument that $HO^\bullet$ is not responsible for the formation of this compound, which is formed by cleavage of two oxygenated carbon atoms.

Conclusions

Photocatalytic degradation of 4-chlorophenol by TiO_2 has a bifurcation in its first step, producing either hydroquinone or 4-chlorocatechol. The hydroquinone pathway has been investigated here. Hydroquinone is mainly oxidized to 1,2,4-benzenetriol. Most of the ring cleavage comes from this compound, though a modest amount of tetraol is observed. Two acyclic six-carbon compounds were observed. The first is identified as **21**, and its very identity argues that it derives from single electron oxidation of **4**, followed by capture by nucleophilic superoxide. The second cleavage product is tentatively identified as **20**. Its structure is consistent with the same cleavage mechanism. The same general mechanism can be used to account for some of the degradation products of several other aromatic compounds, including quinoline, naphthalene, and pyridine. In the benzenetriol system, there is no direct evidence for formation and reaction of the type of bicyclic endoperoxides that are formed in atmospheric oxidation of aromatics or pulse radiolysis, but they also cannot be ruled out.

After the ring opening, the compounds are degraded to smaller and smaller pieces. Pathways to several of them have been suggested. Net hydroxylations, dihydroxylations, hydrations, and decarboxylations are proposed, but many await further study to confirm the direct relationships.

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Experimental Section

Degradations. A 100 mL solution containing the desired concentration of starting material was prepared in water or phosphate buffer (1 mM buffer, pH 4.4, 7.0, and 8.5; pH 2 solution was obtained by using perchloric acid), and 50 mg of TiO_2 was added. Each mixture was dispersed in an ultrasonic bath for 5 min, purged with O_2, and stirred for 20 min in the dark before the irradiation was started. The mixture was continuously purged throughout the experiment. Irradiations were carried out in a Rayonet photochemical reactor with 8 × 4 W "black lights" whose emission is centered at 360 nm. Samples of approximately 1 mL were taken before photolysis and at regular time intervals during the irradiation. They were centrifuged with an Eppendorf Netheler Hinz 5415C and filtered using syringe-mounted 0.2 μm Whatman filters before HPLC analysis. The initial concentration of starting materials for HPLC analysis was 1 mM, and for GC analysis it was 0.2 mM.

For photodegradation of 1,2,4-benzenetriol, the sample solution was first purged by Ar to prevent dark oxidation products before photoreaction. Oxygen was then bubbled through the solution during the photoreaction. The other conditions were the same as above. In addition, blank experiments were carried out for all substrates under the same conditions as indicated above without any lights on.

HPLC Analyses. The concentrations of **2**, **4**, **5**, and **6** were measured by HPLC using a HP 1050 HPLC with diode array detection equipped with a ODS Hypersil C_{18} reversed-phase column (5 μm loop, 200 mm × 2.1 mm). All substances were routinely detected at 220 and 245 nm. The eluent was a phosphate buffer solution (pH 7.0, 5 mM). The flow rate was 0.5 mL min^{-1}. The identification of the intermediates by HPLC was performed by comparing the retention times and UV spectra with those of standards or independently prepared compounds. The concentration of compounds that were not individually identified was calculated using an equation that was derived from calibration measurements for hydroxybenzoquinone. These calculated concentrations of the diacids should thus be taken as only qualitative estimates. The concentration of acids was additionally estimated by comparing the results of the GC analysis with adipic acid as an internal standard material. This gave results similar to the UV approximations.

GC−MS Analyses. Sample Preparation. During irradiation, the pH was regulated to within 0.5 pH units of the original value by periodic addition of solutions of NaOH. After irradiation, the unbuffered solutions (100 mL) were filtered and concentrated to 3 mL under reduced pressure. The solution was acidified with Amberlite IR-120 plus ion-exchange resin (1 g), and the mixture was filtered. Water was removed by freeze-drying.

Reduction of Intermediates. The products formed in the degradations were generally hydrophilic, containing OH, keto, aldehyde, and acid groups. To help identify the compounds and also to identify more intermediates, the samples, concentrated as described above, were sometimes reduced with $NaBH_4$ or $NaBD_4$ before silylation.[55] The reduction conditions were as follows: The above residue was dissolved in methanol (10 mL), and $NaBH_4$ or $NaBD_4$ (30 mg) was added at 0 °C. The reaction was allowed to warm to room temperature and stirred for 3 h. The mixture was acidified with a mixture of 2% hydrochloric acid in methanol and evaporated to dryness in vacuo.

Silylation. The material, reduced or not, was treated with 0.2 mL of anhydrous pyridine, 0.1 mL of hexamethyldisilazane, and 0.05 mL of chlorotrimethylsilane. The reaction was carried out in a 1.5 mL plastic-stoppered vial. The mixture was shaken vigorously for about 60 s and was then allowed to stand for 5 min at room temperature. Precipitate was separated by centrifugation prior to chromatographic analysis.[95]

GC−MS. GC−MS analyses were carried out on a Varian Star 3400CX gas chromatograph using a 25 m DB-5 column, coupled with a Finnigan TSQ700 triple quadrupole mass spectrometer (Finnigan MAT, San Jose, CA) running in single quad mode. The electron energy in the electron impact mode was kept at 70 eV. Resolution was better than 1 mass unit in the entire mass range. For chemical ionization (CI) mode, methane was used as the reagent gas. The data were processed using the Finnigan ICIS software. The temperature program of the column was as follows: at 50 °C, hold time = 4 min; from 50 to 280 °C, rate = 8 °C/min. Similar GC−MS analyses were obtained using a Finnigan Magnum ion trap mass spectrometer coupled to GC with an identical column. It was used in EI mode, but some differences, particularly in relative intensities of fragments, are observed between the ion trap and traditional EI/quadrupole spectra. Data in Table 1 and Figure 5 are from the TSQ spectrometer, but analogous data were obtained on the Magnum. A standard Hewlett-Packard 5890 GC with FID detection and an identical column was also used for routine analysis.

General Instrumentation. TOC determinations were performed on a Shimadzu TOC-5000A total organic carbon analyzer. NMR spectra were obtained at 300 MHz (^1H) and 75 MHz (^{13}C).

Calculations. All ab initio calculations were carried out using the GAMESS suite of programs.[96] Closed-shell molecules were treated at the RHF/6-31G(d) level, fully optimized. Open-shell molecules were optimized with ROHF/6-31G(d). Different conformations of the closed-shell molecules were analyzed using semiempirical methods, and the lowest energy conformation was used as a starting point for optimizations both for the closed- and open-shell species. Electrostatic potentials were determined using the geodesic spheres of Spackman as implemented in GAMESS. A dielectric continuum model (self-consistent reaction field) was used to model the effect of water on the electrostatic potentials; its effect was minimal.

Materials. Hydroquinone, 1,2,4-benzenetriol, ethylene glycol, lactic acid, glycolic acid, oxalic acid, malonic acid, glycolaldehyde, glyoxylic acid monohydrate, maleic acid, succinic acid, fumaric acid, malic acid, tartaric acid, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), chlorotrimethylsilane (TMSCl), pyridine, and sodium borohydride were purchased from Aldrich and used as received. Benzoquinone and 2,5-dihydroxy-1,4-benzoquinone were purified by sublimation. Tartronic acid and β-hydroxypyruvic acid were from Sigma and used as received.

The water employed was purified by a Millipore Milli-Q UV plus system resulting in a resistivity >18 MΩ cm. 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.[97] Other chemicals were of reagent grade and used without further purification.

Identification of Peaks in Table 1−Authentic Samples. The compounds whose TMS derivatives correspond to peaks 1−4, 6−8, 11, 12, 14, 15, 18, and 22 were commercially available. These compounds were obtained and subjected to the silylation and GC−MS analysis as indicated above. Except as noted, the preparations below correspond to the nonsilylated compounds, which were similarly treated. In some cases (as indicated), GC−MS data of the authentic samples were collected only on the Magnum; otherwise MS data are from the TSQ instrument. In either case, retention times and spectra of the authentic sample silyl derivatives and the degradation peaks were convincingly similar.

Peak 5. 3-Hydroxypropionic acid was prepared as described by Negro.[98]

Peak 9. 5-Hydroxymethyl-5*H*-furan-2-one was prepared as described by Alibés.[99]

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Peak 10. *cis*-4-Hydroxypent-2-enoic acid was obtained by reducing 5-hydroxy-5-methyl-5*H*-furan-2-one[100] (0.45 g, 4.9 mmol) in methanol (25 mL) with $NaBH_4$ (0.6 g, 15.7 mmol). The mixture was stirred for 2 h at 0 °C and then acidified to pH 3 with HCl, and the solvent was removed under reduced pressure. The residue was treated with 5 mL of acetone, and a light yellow solid (0.44 g) was obtained after filtering of the precipitate and removal of acetone. A small amount of the *trans* compound (ca. 10%), the corresponding lactone, and CH_3OH contaminated the sample. ^1H NMR (300 MHz, acetone-d_6): δ 6.90 (br s, 2 H, exchanges with D_2O), 6.23 (dd, 1H, $J = 11.7$ Hz, $J = 7.6$ Hz), 5.70 (dd, 1H, $J = 1.5$ Hz, $J = 11.7$ Hz), 5.18 (d ~quint, 1H, $J = 1.5$ Hz, $J = 7.6$ Hz), 1.2 (d, 3H, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, acetone-d_6): 168.7, 154.2, 119.8, 64.8 and 23.1. Mass spectrum of its TMS derivative: *m*/*e* (relative abundance), 73(83), 133(10), 147(100), 171(70), 217(10), 245(62), and 260 (5).

Peak 13. Glyceric acid was obtained by ion exchange from calcium glycerate (100 mg) by dissolving in 5 mL H_2O and stirring with Amberlite IR-120 resin (1 g). The mixture was filtered, and the compound was recovered by freeze-drying.

Peak 16. When functionalized, this compound has two TMS groups, three carbons, four oxygens, and two unsaturations. The two obvious choices are 3-hydroxypyruvic acid and 2-hydroxy-3-oxo-propanoic acid. However, these two compounds are in equilibrium with one another via the ene-diol. Derivatization of commercially available β-hydroxypyruvic acid yielded the same mass spectrum as that observed in the degradations.

Peak 17. 2-Hydroxy-5-oxo-2,5-dihydrofuran-2-carboxylic acid was prepared by singlet oxygen oxidation of 5-trimethylsilylfuran-2-carboxylic acid.[101] This material (3.68 g, 20 mmol), eosin Y (0.06 g), and anhydrous ethanol were placed in a jacketed Pyrex photoreactor. The mixture was irradiated for 15 h with a 200 W incandescent bulb with constant stirring and O_2 bubbling. Water circulating in the jacket kept the solution at ambient temperature. The solvent was removed under reduced pressure to give an oil residue (2.7 g), which was purified by column chromatography on silica gel (ethyl acetate/hexane/acetic acid = 50:50:1) to give a light yellow oil product. ^1H NMR (300 MHz, acetone-d_6): δ 9.25 (br, 2H, exchanges with D_2O), 7.54 (d, 1 H, $J = 5.7$ Hz), 6.37 (d, 1 H, $J = 5.7$ Hz). ^{13}C NMR (75 MHz, acetone-d_6): δ 171.2, 168.1, 153.3, 124.7 and 103.3. FTIR (neat): 3600−2500 br, 1749, 1624, 1230, 1188, 1089, 1057, 925, 821 cm^{-1}. Mass spectrum (EI, 70 eV): *m*/*z* (relative abundance), 44(59), 45(62), 46(28), 54(32), 71(24), 82(10), 99(100), 100(40), 127(8), 144 (5). Mass spectrum of its TMS derivative (EI, 70 eV): *m*/*z* (relative abundance), 73(100), 93(15), 133(20), 147(80), 171(15), 173(13), 201(30), 215(10), 226(10), 273(15), 288(5). The TMS derivative was not stable and was easily decomposed to maleic and fumaric acids. The ring-opened form, i.e., (*Z*)-4-oxopent-2-enedioic acid (oxoglutaconic acid) has previously been reported.[102]

Peak 19. (*Z*)-4-Hydroxypent-2-enedioic acid was prepared by reduction of 2-hydroxy-5-oxo-2,5-dihydrofuran-2-carboxylic acid. $NaBH_4$ (0.28 g, 7.4 mmol) was added to a solution of 2-hydroxy-5-oxo-2,5-dihydrofuran-2-carboxylic acid (0.5 g, 3.4 mmol) in methanol (25 mL) held at 0 °C. The mixture was stirred for an hour and then raised to room temperature for an additional 3 h. The mixture was acidified to pH 3 (apparent) with HCl, and the solvent was removed under reduced pressure. The residue was treated with 10 mL of acetone. After removal of solids and removal of acetone, a light yellow solid (0.45 g, 90%) was obtained. An analytical sample was obtained by dissolving the material in 1 mL of methanol and adding 5 mL of acetone dropwise. Precipitates were again removed, and the solvent was evaporated to yield 0.15 g (30%) of a white solid. ^1H NMR (300 MHz, D_2O): δ 6.10 (dd, 1 H, $J = 12$, 6.6 Hz), 6.04 (d, 1 H, $J = 12$ Hz), 5.38 (d, 1 H, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, D_2O): δ 176.4, 171.5, 141.9, 124.8 and 68.8. FTIR (neat): 3600−2800 br, 2608, 1733, 1699, 1256, and 1097 cm^{-1}. Mass spectrum (EI, 70 eV): *m*/*z* (relative abundance), 44(100), 45(35), 55(44), 73(15), 74(12), 85(26), 101(33), and 102(16). CI, 146. Mass spectrum of its TMS derivative: *m*/*z* (relative abundance), 73 (100), 133(10), 147(24), 156(15), 217(10), 245(6), 257 (8), 317 (10), 347(45), and 362 (2).

Peak 20. As discussed in the results section, (*Z*)-4-oxohex-2-enedioic acid (maleylacetic acid) was not obtained in pure form. As outlined in the paragraphs below, first the silylated derivative of (2-hydroxy-5-oxo-2,5-dihydro-furan-2-yl)-acetic acid, i.e., compound **14**, was obtained as part of a mixture. The silyl groups were hydrolyzed to yield the free diacid, which was trapped as its trisilyl derivative, i.e., **15**.

2′-Furylacetic acid (1.26 g, 10 mmol), eosin Y (30 mg), vanadium pentoxide (10 mg), anhydrous pyridine (90 mL), and 1,1,1,3,3,3-hexamethyldisilazane (10 mL) were placed in a jacketed Pyrex photoreactor. Visible irradiation was carried out at room temperature, and a second aliquot of eosin Y was added when the red color was bleached to yellow. After 16 h, the starting material was consumed. After centrifugation and decanting, the solvent was removed to give a red oil residue (1.30 g) which solidified on standing. This contained the compound characterized below, but partial purification was carried out by distillation. A pale yellow oil (0.25 g) was collected with bp = 80 °C at 250 mTorr in a Hickman head. As determined by NMR, this contained a mixture of compounds; about 50% of the mixture was compound **14**. The spectrum was assigned by analogy to all the related compounds described herein. ^1H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, 1 H, $J = 5.7$ Hz), 6.10 (d, 1 H, $J = 5.7$ Hz), 3.10 (d, 1 H, $J = 15.3$ Hz), 2.78 (d, 1 H, $J = 15.3$ Hz), 0.30 (s, 9 H), 0.15 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 168.3, 155.8, 121.7, 103.4, 46.6, 1.2, and 0.3.

Approximately 200 mg of the above mixture was stirred in ice-cooled phosphate buffer (2 mL, pH 3). The solution was extracted with chilled ether (6 × 2 mL). The organic extract was dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield 80 mg of a pale yellow oil. Again, as determined by NMR, this was a mixture. About one-third of the mixture was maleylacetic acid, **13**. ^1H NMR (300 MHz, DMSO): δ 7.57 (d, 1 H, $J = 5.7$ Hz), 6.25 (d, 1 H, $J = 5.7$ Hz), 2.94 (d, 1 H, $J = 15$ Hz), 2.84 (d, 1 H, $J = 15$ Hz). After resilylation under standard conditions, peak 20 was obtained with matching retention time and mass spectrum. MS (EI, 70 eV): *m*/*z* (relative abundance), 73(60), 147(20), 257(100), 315(8), and 359(10). This mass spectrum was essentially identical to that of the TMS derivative of (*E*)-4-oxohex-2-enedioic acid (fumarylacetic acid),[63] though slightly different GC retention times were observed.

Peak 20, Alternate Preparation. To a magnetically stirred solution of 5 mL of HOAc, 3.85 mL of 32% of HOOAc (1.24 g, 16.25 mmol), and 1 mg of ferric acetate at 25 °C was added, at a rate of approximately 1 drop per minute over about 5 h,[103] 10 mL of a HOAc solution containing 0.63 g (5 mmol) of 1,2,4-benzenetriol. The reaction mixture was stirred for an additional 1 h, and then the solvent was removed by rotary evaporation to give a dark residue (0.6 g). Crude NMR indicated the presence of **13** as reported above, with about 60% of the mixture being **13** and the *trans* isomer also being easily identified as about 20% of the mixture. Further attempts to purify the mixture were either ineffective or resulted in the decarboxylation of **13**. ^1H NMR (300 MHz, acetone-d_6): δ 7.61 ppm (d, $J = 5.7$ Hz, 1H), 6.17 (d, $J = 5.7$ Hz, 1H), 3.09 (d, $J = 15.6$ Hz, 1H), 2.97 (d, $J = 15.6$ Hz, 1H). ^{13}C NMR (75 MHz): δ 172.3, 170.2, 155.3, 123.5, 105.9 and 42.9 ppm. Mass spectrum of its TMS derivative (**15**): *m*/*z* (relative abundance), 73(60), 147(20), 257(100), 315(8), and 359(10).

Peak 21. 2-Hydroxyglutaric acid was prepared by reduction of 2-oxoglutaric acid with $NaBH_4$ as previously described.[104] ^1H NMR (300 MHz, D_2O): δ 4.40 (dd, 1 H, $J = 7.8$, 4.5 Hz),

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2.58 (2 H, appears approximately as two overlapping triplets), 2.11−2.28 (m, 1 H), and 1.94−2.07 (m, 1 H). ^{13}C NMR (75 MHz, D_2O): δ 177.6, 177.5, 69.3, 29.7, and 28.7 ppm. Mass spectrum (Magnum) of its TMS derivative: *m*/*z* (relative abundance) 73(100), 129(60), 147(55), 203(35), 247(65), 275(15), 321(10), 349(30).

Peak 23. The identity of peak 23 as the TMS derivative of (*E*)-4-hydroxypent-2-enedioic acid was confirmed by its mass spectrum, which was virtually identical to that of peak 19, and was rigorously confirmed as the Z isomer.

Peak 24. 4,5,6-Trihydroxy-(*Z*)-hex-2-enoic acid was prepared in three steps from 5′-trimethylsilylfuran-2′-yloxoacetaldehyde.[105] The glyoxal (1.2 g, 6.1 mmol) was reduced with $NaBH_4$ as previously described. The resulting residue was purified by silica chromatography (hexane/ethyl acetate/ethanol = 75:20:5) to provide 2-(1,2-dihydroxyethyl)-5-trimethylsilylfuran in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.54 (d, 1 H, $J = 3.2$ Hz), 6.26 (d, 1 H, $J = 3.2$ Hz), 4.81 (∼q, 1 H, $J_1 = 4.8$ Hz), 4.01 (d, 1 H, $J = 4.8$ Hz, exchangeable with D_2O), 3.82 (∼t, 2H, $J = 4.8$ Hz), 3.60(t, 1H, $J = 4.8$ Hz, exchangeable with D_2O) and 0.24 (s, 9 H, TMS). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.4, 157.9, 120.5, 107.0, 68.8, 65.4, 1.45.

A solution of 2-(1,2-dihydroxyethyl)-5-trimethylsilylfuran (1 g, 5.0 mmol) and eosin Y (30 mg) in ethanol was irradiated with visible light as above for 7 h. After removal of the solvent, purification by silica chromatography (hexane/ethyl acetate/acetic acid = 10:89:1) gave a yellowish oil (0.75 g, 74%) that was an approximately 2:1 mixture of two diastereomers of 5-(1,2-dihydroxyethyl)-5-hydroxy-5*H*-furan-2-one. ^{1}H NMR (300 MHz, acetone): δ 7.44 and 7.41 (each is d, 7.44 is the major diastereomer, 1 H, $J = 5.7$ Hz), 6.6, (br, 1 H, exchangeable with D_2O), 6.15 (d, 1 H, $J = 5.7$ Hz), 4.5 and 4.1 (br s, 4.5 is major diastereomer, 1 H, exchangeable with D_2O), 3.84 (m, 3 H). ^{13}C NMR (75 MHz, acetone, minor diastereomer in parentheses): δ (171.3) 171.2, (154.8) 154.3, 124.2 (123.9), 109.3 (109.1), 74.9 (74.0), and 63.4 (63.2).

Finally, (*Z*)-4,5,6-trihydroxy-2-hexenoic acid was prepared by reducing 5-(1,2-dihydroxyethyl)-5-hydroxy-5*H*-furan-2-one (0.14 g, 0.88 mmol) with $NaBH_4$ as previously described, save that the solvent was removed at 0 °C. After the residue was washed with cold acetone, a pale yellow oil was obtained (0.12 g). This is a mixture of two diastereomers in approximately equal quantity and some CH_3OH. Attempts to obtain analytically clean samples by column chromatography were unsuccessful, and the compound readily dehydrates on even gentle warming.^{1}H NMR (300 MHz, acetone): δ 6.37 (dd, 1 H, $J = 11.1$, 3.3 Hz) and 6.33 (dd, $J = 11.1$, 3.3 Hz), 5.91 (dd, 1 H, $J = 11.1$, 1.2 Hz) and 5.87 (dd, $J = 11.1$, 1.2 Hz), 5.08 (m, 1 H), 3.60−3.85 (m, 3 H). ^{13}C NMR (75 MHz, acetone): δ 168.3 (168.6), 150.0 (150.8), 121.7 (121.1), 75.4 (75.6), 69.4 (69.6), 64.2 (64.0). The ^{13}C NMR spectrum of the *trans* isomer has been reported previously.[106] Mass spectrum of its TMS derivative (ion trap): *m*/*z*, 73 (100), 147(30), 218(8), 255(5), 271(20), 320(5), 345(20), 407(3), 435(15), and 450(2).

After several hours of exposure to vacuum at room temperature, about 50% of the material had dehydrated to 5-(1,2-dihydroxyethyl)-5*H*-furan-2-one (also still two diastereomers). Complete dehydration could be accomplished by warming the neat sample to 50 °C for 30 min. ^{1}H NMR (300 MHz, wet acetone): δ 7.81 ppm (dd, 1 H, $J = 5.7$, 1.8 Hz) and 7.72 (dd, $J = 5.7$, 1.8 Hz), 6.15 (dd, 1 H, $J = 5.7$, 1.8 Hz) and 6.13 (dd, $J = 5.7$, 2.1 Hz), 5.16 (dt, 1 H, $J = 5.4$, 1.8 Hz) and 5.23 (dt, $J = 3.6$, 1.8 Hz), 3.65−3.91 (m, 3 H). ^{13}C NMR (75 MHz, acetone): δ 173.8 (173.6), 156.5 (156.3), (122.3) 122.2, 84.8 (84.5), 73.2 (72.4), (63.9) 63.8.

Peak 25. Both isomers of 2,4-dihydroxyglutaric acid were prepared according to a reported method.[107] Peak 25 appeared to be the *meso* isomer.

Peak 26. Benzene-1,2,4,5-tetraol was prepared by reduction of 2,5,-dihydroxy-1,4-benzoquinone with sodium hyposulfite according to a reported method.[108]

Peak 27. All three isomers of 2,3,4-trihydroxypentanedioic acid were prepared by oxidation of ribose, xylose, and arabinose, and the saccharic acids of these sugars represent the peaks at 16.63, 16.71, and 16.91 min, respectively. The method was that described by Gall.[98]

Peak 28. The compound 2,2′,4,4′,5,5′-biphenylhexol was not prepared, and its precise structure is an educated guess. This compound has the correct molecular formula to match the peak and is chemically reasonable from 1,2,4-benzenetriol.

Peak "a". The mass spectrum of this peak is 73(100), 147(48), 257(20), and 272(18). The molecular weight of 272 was confirmed by CI. The compound is not reduced by $NaBH_4$ and also appears as a small peak in the degradation of **11**. It has two TMS groups, and its proposed molecular formula is $C_5H_2O_4(TMS)_2$. A suggested structure is a disilylation product of a tautomer of 5-oxo-2,5-dihidrofuran-2-carboxylic acid, e.g., disilylated 5-hydroxyfuran-2-carboxylic acid. This might be a reduction product of **11**. However, attempts to synthesize 5-oxo-2,5-dihidrofuran-2-carboxylic acid were unsuccessful, and this structure was not verified.

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Supporting Information Available: Copies of ^{1}H spectra for compounds giving rise to peaks 10, 17, 19, 20, and 24 of Table 1, including selected synthetic precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

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