

Photochemical Acetalization of Carbonyl Compounds in Protic Media Using an in Situ Generated Photocatalyst

H. J. Peter de Lijser* and Natalie Ann Rangel

Department of Chemistry and Biochemistry, California State University Fullerton,
Fullerton, California 92834-6866

pdelijser@fullerton.edu

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Carbonyl compounds are conveniently converted into their corresponding dimethyl acetals in good yields and short reaction times by means of a photochemical reaction in methanol with a catalytic amount of chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone, CA) as the sensitizer. Using aldehydes gives better results than using ketones, which also tend to form enol ethers as side products. These results are similar to those of simple acid-catalyzed acetalization reactions, suggesting the involvement of a photochemically generated acid. On the basis of steady state and laser flash photolysis data the reaction is proposed to involve the in situ generation of a photocatalyst (2,3,5,6-tetrachloro-1,4-hydroquinone, TCHQ) via reaction of CA with the solvent. The acetalization process is initiated by ionization of TCHQ, followed by loss of a proton to the solvent or the carbonyl, which starts a catalytic reaction. The photocatalyst is regenerated via a disproportionation reaction.

Introduction

Carbonyl compounds are essential building blocks of organic chemistry because of their chemical versatility. Often this functional group must be protected while carrying out a series of steps, and acetalization is one of the preferred methodologies.¹ Most often these reactions are acid-catalyzed, but this does have its drawbacks as other functionalities in the molecule may be acid-sensitive. As a result, many other methodologies have been developed and the search for new and improved methods continues.^{1,2} Photochemistry provides an elegant way to access intermediates and pathways that are often not available or difficult to reach when using ground-state reactions. For example, the development of photoremovable groups has been and still is of great interest.³ Several photochemical methods for the deprotection of carbonyl compounds have also been reported,⁴ but few if any methods for the photochemical protection of carbonyl compounds are known. Although the formation of acetals from carbonyl compounds upon irradiation in hydroxylic solvents has been reported, this process has not found

widespread application, most likely because it is considered an abnormality caused by (acidic) impurities. To achieve good conversions and yields for this type of reaction, a photosensitized process generating an acidic species would be desirable. Quinones are commonly used as photosensitizers, and irradiation of these types of compounds in hydroxylic solvents results in the formation of hydroquinones (hydroxyarenes). These photoproducts may undergo photochemical reactions themselves as well. One particularly interesting aspect of certain hydroxyarenes, as first noted by Förster,^{5a} is that their excited states (S_1) are (much) more acidic than the groundstate (S_0).⁵ For example, for 1-naphthol (**1**) the pK_a values are 9.4 (S_0) and -0.2 (S_1).^{5d} Species that exhibit such behavior are commonly referred to as photoacids. They are used in a variety of processes including polymerization, the degradation of polymers, transformation of functional groups, photoresists, and optical lithography.⁶ In recent years many different types of photoacids have been

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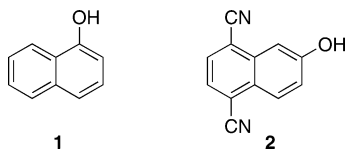
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investigated. Much of the research has focused on the development, behavior, and physical properties of so-called “super” photoacids such as 5,8-dicyano-2-naphthol (**2**; $pK_a^* \approx -4.5$).⁷



A second option for generating acidic species would be via ionization of a neutral substrate. Removal of a single electron from a molecule results in the weakening of a chemical bond, and the pK_a of the radical cation is often several orders of magnitude smaller than that of the neutral species.⁸ One potentially attractive set of candidates would be the phenols, as they can be generated from quinones and are known to undergo fast deprotonation upon ionization.⁹

Recently we found that irradiation of carbonyl compounds in the presence of quinone sensitizers in protic solvents resulted in the formation of acetals.¹⁰ These results are not consistent with the known photochemistry of either the carbonyl compounds or the quinones. To find out whether these observations were due to impurities or other artifacts, we have undertaken a more extensive investigation on which we here report. The results are most consistent with the in situ formation of a photocatalyst, which initiates the acetalization process. The major advantage of this system is that the photocatalyst is regenerated continuously.

Results and Discussion

Steady-State Photolysis of Aldehydes and Ketones with Chloranil in Protic Solvents. Photolysis of *O*-benzylacetophenone oxime and chloranil (CA) in acetonitrile results in the formation of acetophenone and benzaldehyde. When using a polar protic solvent such as methanol, no benzaldehyde is observed but rather benzyl alcohol as well as traces of benzaldehyde dimethylacetal.¹⁰ Initially, benzyl alcohol was thought to be the product of a photochemical reaction of benzaldehyde with methanol; however, this was shown not to be true in a separate experiment. Interestingly, irradiation (60 min) of a solution of benzaldehyde and CA in methanol results in the quantitative formation of the dimethyl acetal (Table 1, entry 1). Further studies on this reaction have shown that even a catalytic amount (1 mol %) of CA (entry 6) can achieve a significant conversion of the aldehyde and yield of the acetal. The reaction can be completed in as little as 15 min when using benzaldehyde and a higher concentration of CA. Similar results are

TABLE 1. Summary of Results for the Photolysis of Benzaldehyde in Protic Solvents^a

entry	sensitizer	time (min) ^b	solvent	conversion (%) ^c	acetal (%) ^c
1 ^d	CA	60	MeOH	96	100
2 ^d	CA	30	MeOH	97	100
3 ^d	CA	15	MeOH	96	100
4	CA	30	MeOH	97	100
5 ^e	CA	30	MeOH	97	100
6 ^f	CA	30	MeOH	89	100
7	CA	30	4:1 MeCN–MeOH	89	100
8	CA	30	EtOH	82	100
9	CA	30	4:1 MeCN–EtOH	63	100
10	XA	30	4:1 MeCN–MeOH	82	100
11	TCHQ	30	4:1 MeCN–MeOH	78	100
12	DCNQ	30	4:1 MeCN–MeOH	74	100

^a Reactions were carried out in Pyrex glass using a Rayonet photochemical reactor equipped with sixteen 350 nm light bulbs; the benzaldehyde concentration was 0.015 M unless indicated otherwise; the sensitizer concentration was 0.005 M unless indicated otherwise. ^b Irradiation time. ^c Conversions and yields were determined by calibrated GC/FID. ^d [Sensitizer] = 0.015 M. ^e [Benzaldehyde] = 0.050 M. ^f [Benzaldehyde] = 0.500 M.

obtained when using ethanol as the solvent (or as a mixture with MeCN; entries 8 and 9), but using *i*-PrOH gives very poor results. When using ethylene glycol as the solvent some acetal is observed; however, there was significant overlap of the reactants and the solvent on the GC, making a detailed analysis impossible.

Other photocatalysts that were tested include duroquinone (DQ), 1,4-naphthoquinone (NQ), phenanthrenequinone (PQ), xanthone (XA), 2,3-dichloro-1,4-naphthoquinone (DCNQ), and tetrachloro-*p*-hydroquinone (TCHQ). From the results listed in Table 1 (entries 10–12) it can be seen that under a set of standard conditions most of these sensitizers give results similar to CA; however, using DQ, NQ, and PQ did not result in any conversion of the carbonyl compound or in acetal formation. The results are reproducible as long as an appropriate photocatalyst is present in the mixture. In the absence of CA or any other photocatalyst, virtually no acetal is formed and the carbonyl conversion is significantly lower. The solubility of CA in MeOH is low, and the majority can be recovered afterward. TCHQ dissolves readily in MeOH and can be detected afterward. A trace of CA was also detected. Irradiation of the aldehyde and CA in the presence of a base (sodium bicarbonate) does not result in any reaction, suggesting the involvement of a photo-generated acid. The reaction also proceeds when using 420 nm light bulbs but is somewhat less efficient (52% yield after 30 min). Finally, irradiation of a mixture containing the acetal and CA in 4:1 MeCN–MeOH does not result in any reaction, i.e., the process is not reversible under the conditions of the reaction. It must be noted that small amounts of water do influence the reaction significantly. For example, photolysis of a solution containing the acetal and CA in MeCN did result in the formation of the aldehyde. This is consistent with a report by Sankararaman,¹¹ who reported that DDQ can be used for the photoinduced deprotection of thioacetals and ketals. Also, when benzaldehyde and CA were irradiated in 95% EtOH, only a small amount of the acetal was formed and most of the benzaldehyde was recovered.

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TABLE 2. Results from Photosensitized Reactions of Aldehydes in Methanol^a

entry	aldehyde	conversion (%) ^b	acetal yield (%) ^b
1	benzaldehyde	89	100
2	hexanal	96	100
3	cyclohexanecarboxaldehyde	97	100
4	3,3-dimethylbutyraldehyde	94	100
5	phenylacetaldehyde	81	100
6	<i>o</i> -tolualdehyde	73	100
7	2,6-dimethylbenzaldehyde	62	100
8	dodecanal	93	100
9	<i>trans</i> -cinnamaldehyde	47	100
10	hydrocinnamaldehyde	98	100

^a [CA] = 0.005 M; [aldehyde] = 0.015 M; all solutions were irradiated for 30 min. ^b Conversions and yields were determined by calibrated GC/FID.

To determine the generality of this reaction, a number of carbonyl compounds were tested under standard conditions. The results for the aldehydes are listed in Table 2, and those for the ketones are shown in Tables 3 and 4.

None of the aldehydes or ketones tested, with the exception of *trans*-cinnamaldehyde, absorb any light above 300 nm. The only species absorbing light under the conditions of the reaction (Pyrex tubes) is CA. It can be seen that most aldehydes typically react fast and give high yields of the corresponding acetal. The decreased reactivity of *o*-tolualdehyde (entry 6) and 2,6-dimethylbenzaldehyde (entry 7) suggest that either steric effects or electronic effects are important. Electronic effects are known to be important in acetalization reaction, which results in ketones being less reactive than aldehydes. However, it remains to be seen whether the *o*-methyl groups cause a steric effect and/or an electronic effect. The results for *trans*-cinnamaldehyde (entry 9) are interesting. Analysis of the product mixture revealed the presence of both the *cis*- and the *trans*-aldehydes (1:10 ratio), as well as the *cis*- and the *trans*-acetals (1:1.2 ratio). It has been reported that irradiation of *trans*-cinnamaldehyde in MeOH results in the formation of *cis*- and *trans*-cinnamaldehyde as well as the *cis*- and *trans*-dimethylacetals.¹² However, in our laboratory, irradiation of *trans*-cinnamaldehyde without CA present (in 4:1 MeCN–MeOH) resulted only in some *trans*–*cis* isomerization. These results suggest that formation of the acetal is an acid-catalyzed process rather than a photochemical process. Adkins and Hartung reported that extended conjugation results in a lower reactivity for acetalization.¹³ Our results are in agreement with that observation; *trans*-cinnamaldehyde reacts significantly more slowly than hydrocinnamaldehyde.

Different results are obtained when using ketones. A first set of experiments with cyclohexanone gave results similar to those observed for benzaldehyde (Table 3). The conversion was much larger when using pure methanol as the solvent rather than an acetonitrile–methanol mixture. The corresponding enol ether was always present, except when the reaction was carried out in 4:1 MeCN–MeOH. When cyclohexanone dimethylacetal was irradi-

TABLE 3. Summary of Results for the Photolysis of Cyclohexanone in Protic Solvents^a

entry	sensitizer	time (min) ^b	solvent	conversion (%) ^c	acetal (%) ^c	enol ether (%) ^c
1 ^d	CA	30	MeOH	90	92	8
2	CA	30	MeOH	95	85	15
3	CA	30	4:1 MeCN–MeOH	44	>99	<1
4	TCHQ	30	MeOH	74	73	26

^a Cyclohexanone concentration was 0.015 M; the sensitizer concentration was 0.005 M unless indicated otherwise. ^b Irradiation time. ^c Conversions and yields were determined by calibrated GC/FID. ^d [Sensitizer] = 0.015 M.

TABLE 4. Results from Photosensitized Reactions of Ketones in Methanol^a

entry	ketone (%)	conversion (%) ^b	acetal (%) ^b	enol ether (%) ^b
1a	cyclopentanone	25	100	
1b	1-indanone	18		
1c	2-indanone	70	56	44
2a	cyclohexanone	95	85	15
2b	4- <i>tert</i> -butylcyclohexanone	91	67	33
2c	2-methylcyclohexanone	32	100	
2d	1-decalone	<5 ^c		
2e	2-decalone	61	<i>d</i>	<i>d</i>
2f	α -tetralone	<5 ^c		
2g	β -tetralone	44	6	94
2h	camphor	36	100	
2i	[3,2,1]-bicyclo-2-octanone	72	54	46
2j	2-adamantanone	87	100	
3a	cycloheptanone	12		
3b	1-benzosuberone	<5 ^c		
4	cyclooctanone	<5 ^c		
5	3-pentanone	35		
6	dibenzyl ketone	10		
7a	acetophenone	28		
7b	2,2,2-trifluoroacetophenone	<5 ^c		
8	benzylacetone	30		

^a [CA] = 0.005 M; [ketone] = 0.015 M; irradiated for 30 min in MeOH. ^b Conversions and yields were determined by calibrated GC/FID. ^c Within the limits of experimental error; no conversion of starting material. ^d Product mixture consisted of several compounds. Minor product was the acetal and major product was the enol ether, but quantification was not possible because of significant peak overlap.

ated in the presence of a mixture containing the ketone (5%), acetal (80%) and enol ether (15%) was obtained.

Not all ketones react under these conditions. From Table 4 it can be seen that, even when using methanol as the solvent, several ketones (1-decalone, α -tetralone, 1-benzosuberone, cyclooctanone, and 2,2,2-trifluoroacetophenone) do not react at all (no conversion is observed). Several other ketones do react but do not form the acetal in any significant amount. In some cases small amounts of dimerized products (as determined by GC/MS) were formed instead, but often no distinct product(s) were observed. In contrast, certain ketones, including cyclohexanone, 4-*tert*-butylcyclohexanone, and 2-adamantanone give excellent results. Often, the formation of an enol ether is also observed; only in the cases of cyclopentanone, 2-methylcyclohexanone, camphor, and 2-adamantanone was the acetal the only product formed.

The most reactive substrates seem to be those with six membered rings (entries 2a–2j). Steric effects are important, as can be seen from entries 2c, 2d, and 2f. Rigidity of the carbon skeleton is not of major importance;

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even though 2-adamantanone gives the best results in terms of acetal formation, cyclohexanone itself reacts rapidly and forms the acetal in good yield. Other more rigid structures such as the decalones, camphor, and bicyclo[3.2.1]octan-2-one react poorly or give large amounts of the enol ether. The observed reactivity of camphor and bicyclo[3.2.1]octan-2-one is interesting and could possibly be a result of the presence of the five- and seven-membered rings in these compounds. Substrates with five-membered rings are less reactive compared to six-membered rings. Cyclopentanone reacts to give the acetal as the only product albeit in low yield. Attaching an aromatic ring in the β -position increases the reactivity, but now the product mixture contains both the acetal and the enol ether in a 1:1 ratio. These trends are similar to those observed for cyclohexanone and the tetralones. Substrates with seven-membered rings do not react; the exception would be bicyclo[3.2.1]octan-2-one, although this is more likely to be considered a substituted six-membered ring. These results are in reasonable agreement with those from the acid-catalyzed acetalization of carbonyl compounds reported by Brown¹⁴ and Djerassi.¹⁵ In both studies it was observed that five- and seven-membered rings react more slowly than six-membered rings.

Steric effects are of major importance in these reactions, as seen from the results of the reaction of acetophenone. No reaction occurred, which is a dramatic difference compared to benzaldehyde. It is well-known that the acid-catalyzed acetalization of ketones is slower than that of aldehydes, although the reaction can be forced in the direction of the acetal.¹⁶ For example, Roelofsen and van Bekkum reported that the acetalization of ketones required larger amounts of the acid catalyst in order to proceed.¹⁷ We have not yet been able to increase the yield of acetal for unreactive ketones by increasing the amount of CA. Irradiation of mixtures containing acetophenone and various amounts of CA (0.005, 0.015, and 0.025 M) did not result in the formation of the acetal. The significant (steric) effect of a methyl group can also be seen from the reactivity of 3-pentanone, dibenzyl ketone, and benzylacetone. Even though the phenyl group is further away from the carbonyl or even completely absent, still no significant reaction can be observed. This is consistent with a study by Wiberg et al., which concluded that alkyl substitution stabilizes a carbonyl group and destabilizes the acetal.^{18a}

In addition to the steric effects, we were also interested to see if electronic effects were important for the reactions of ketones. It is known that the introduction of electron-accepting groups destabilize the carbonyl group and favor formation of the acetal.^{18b} Preliminary experiments suggest that electronic effects are not predominant in these reactions. For example, irradiation of 2,2,2-trifluoro-

acetophenone does not yield any acetal, confirming the predominance of steric effects in these reactions.

Mechanistic Interpretation. The most likely explanation for these results is the in situ photogeneration of an acidic species, which catalyzes the acetalization. Others investigators have also observed the formation of acetals in the photolysis of carbonyl compounds in protic solvents.^{19,20} In these particular cases it was proposed that the acetal is formed by means of an acid-catalyzed process due to impurities in the solvent or via a photoacid generation process. The formation of the acetal was usually suppressed when using base-washed glassware or when the reaction was carried out in the presence of sodium bicarbonate.^{19a} Kim and co-workers observed the formation of 3-methoxycyclohex-2-en-1-one from photolysis of 1,3-cyclohexanedione and *p*-benzoquinone in methanol and proposed an enol radical cation intermediate.^{19c} Hill and co-workers observed the formation of acetals upon photolysis of α -aryloxyacetones; however, the reactions were not selective and the yields were generally low.²⁰ Clearly, the results reported here cannot be due to impurities as the presence of a photocatalyst gives completely different (clean and reproducible) results. More evidence for the involvement of a photogenerated acidic species came from an experiment in which a sample was irradiated for only 1 min and then placed in the dark. Analysis of the sample before and after storage in the dark clearly shows that the reaction continued on, although it was less efficient compared to a sample that was irradiated for 30 min. An interesting observation was the fact that almost identical results are obtained when using CA or TCHQ, suggesting that the latter is formed from CA and acts as the acid. This is consistent with earlier observations. It was reported that irradiation of CA in methanol or ethanol results in the formation of TCHQ (major) and trichlorohydroxy-*p*-benzoquinone (minor).²¹ Another important piece of information is the fact that the reaction only requires a catalytic amount of CA. We will discuss three mechanistic schemes, each of which can explain these results.

The results presented in the tables above are very similar to those observed for the classic acid-catalyzed acetalization of carbonyl compounds.¹ As such, a simple mechanism generating an inorganic acid such as HCl must be considered first. It has been reported that photolysis of CA in aldehydes results in the formation of acylhydroquinones and generates hydrogen chloride (Scheme 1).²²

In order for HCl to be formed, the acyl radical must add to a chlorine-substituted ring carbon. Studies on CA and different aldehydes have shown, however, that the major product forms via reaction at the oxygen to produce an ester. For example, the reaction of CA with acetaldehyde produces tetrachloroquinol monoacetate (73%) and trichloroacetylquinol (1%).²² The reaction of CA with benzaldehyde reportedly produced only the benzoate

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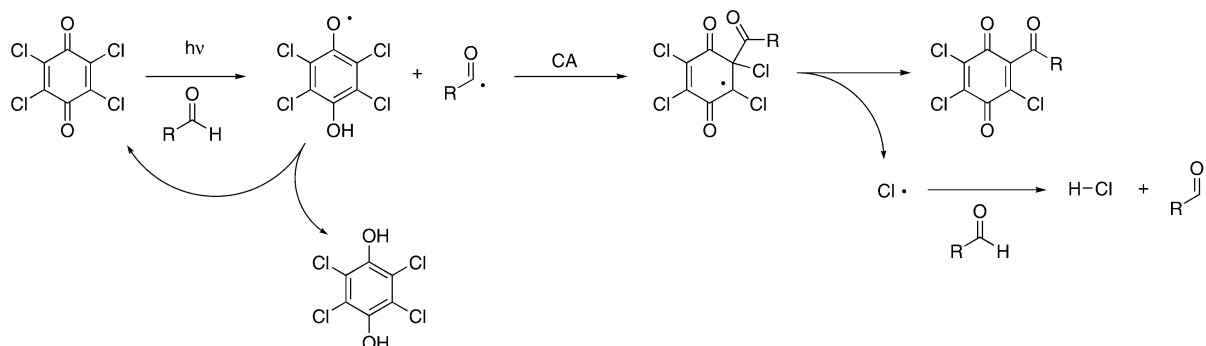
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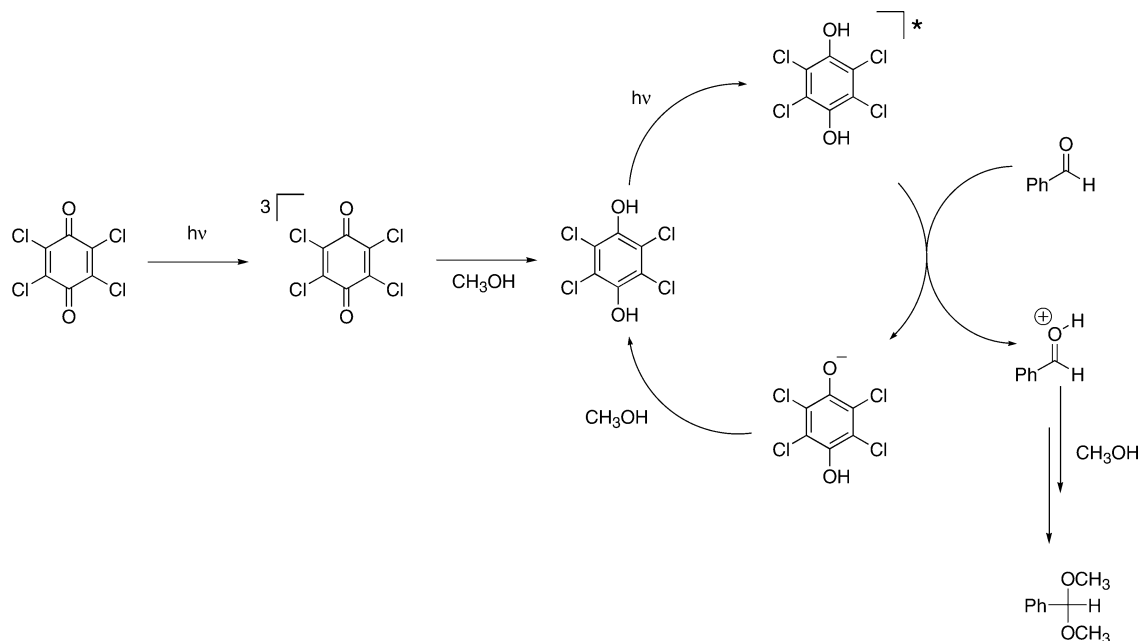
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SCHEME 1



SCHEME 2



ester.²³ Although under our conditions, on the basis of the concentrations of MeOH and the aldehyde used, this reaction is unlikely, it must be noted that in order for the acetalization to occur, only a catalytic amount of HCl is required. It cannot be ruled out that when using CA as the sensitizer side reactions occur that produce this catalyst. Once it forms, it could easily be regenerated, not requiring any further side reactions.

One observation that does not support this mechanism, however, is the fact that almost identical results are obtained when using xanthone (XA) instead of CA. XA is not expected to form such acid catalysts. This observation, together with the argument that the concentration of the aldehyde is more than 1600 times smaller than that of the solvent, suggest that this mechanism is most likely not valid.

A second possible mechanism, which incorporates the observation that quinones are reduced to quinols upon photolysis in hydroxylic solvents, is shown in Scheme 2.

Photolysis of CA in methanol results in the formation of TCHQ.²¹ Excitation of this hydroquinone generates an acidic species that protonates the carbonyl compound (directly or indirectly via a proton carrier such as MeOH).

Further reaction of this protonated species with the solvent yields the acetal.

There is ample precedent for the enhanced acidity of phenolic species upon irradiation. For example, 2-cyanophenol has an excited-state pK_a of 0.66 (compared to a pK_a of 6.97 in the groundstate).²⁴ The pK_a^* of TCHQ is not known, and therefore it remains to be seen whether it is acidic enough to protonate either MeOH or a carbonyl group. The pK_a value for $MeOH_2^+$ is -2.2 (estimated),²⁵ whereas those of $C=OH^+$ species are estimated to be between -6 and -10 ,^{25,26} depending on the structure. For example, the conjugate acids of cyclohexanone and benzaldehyde have pK_a 's of -6.8 and -7.1 , respectively. On the other hand, it must be noted that weaker acids are also capable of catalyzing the acetalization of carbonyl compounds, although it often requires removal of water from the mixture in order to push the equilib-

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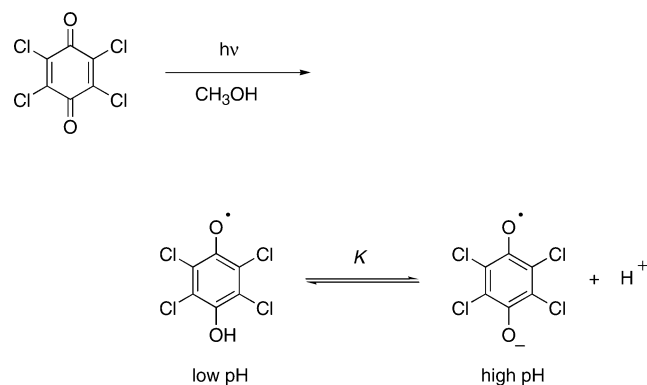
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rium in the direction of the acetal. In another example, *N*-hydroxybenzenesulfonamide ($pK_a = 9.26$) was used successfully as a catalyst for the acetalization of *p*-chlorobenzaldehyde, but its catalytic activity was suggested to be a result of its combined nucleophilicity and leaving group ability.²⁷

To find out whether weaker photoacids such as 6-cyano-2-naphthol, 6CN2 ($pK_a^* = 0.2$), and 2-cyanophenol, 2CP ($pK_a^* = 0.66$), can act as the photocatalyst, a MeOH solution containing benzaldehyde and 6CN2 or 2CP was irradiated for 30 min. Neither reaction yielded any acetal, even when the concentration of the photoacid was increased. These results suggest that the excited states of 2CP and 6CN2 are not strong enough to protonate either the solvent or the carbonyl. From these observations, it follows that (i) TCHQ is either a much stronger photoacid than 2CP and 6CN2, or (ii) the reaction occurs via a different mechanism. Because the pK_a^* of TCHQ is unknown, we have focused our attention on a third possible pathway, which involves an electron transfer (ET) step.

Flash photolysis studies have shown that irradiation of chloranil (and other quinones) in hydroxylic solvents results in the formation of the semiquinone radical, which exists in equilibrium with the chloranil (quinone) radical anion:²⁸



In ethanol, the equilibrium favors the semiquinone radical ($K = 1 \times 10^{-6}$ M), and the rate constant for the recombination reaction was estimated to be $7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.^{28b} The decay of the semiquinone radical was proposed to occur via a disproportionation reaction rather than reaction with the solvent. The lifetime of the semiquinone radical is on the order of milliseconds, which is consistent with our own observations. The species observed upon flash photolysis (355 nm) of a solution containing CA and an electron donor (acetophenone oxime) in MeOH is long-lived (no significant decay of the signal on the microsecond time scale was observed; Figure 1). The signal is attributed to that of the semiquinone radical, which is formed via reaction of the radical anion with the solvent.¹⁰ Considering these studies, the mechanism shown in Scheme 3 can be proposed.

In principle, two catalytic cycles are available. The first step in both sequences involves formation of the semi-

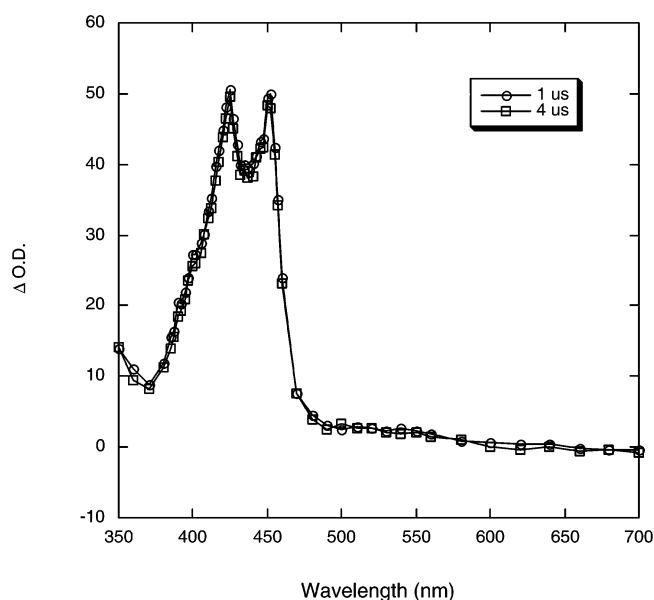
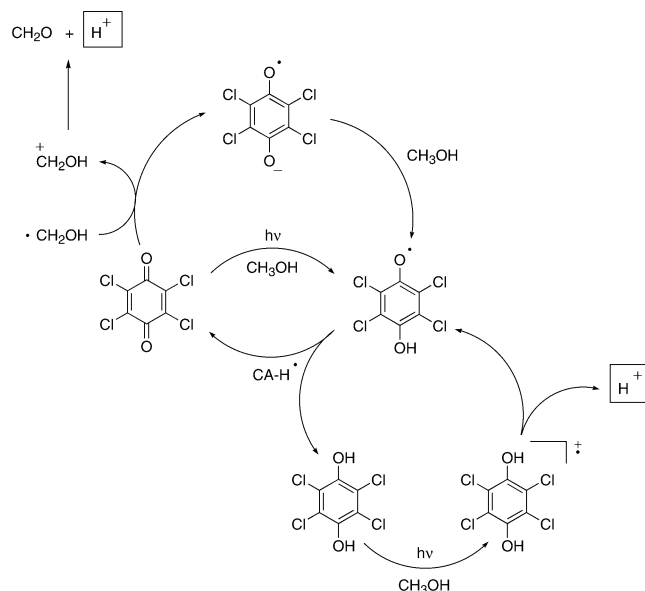


FIGURE 1. Absorption spectrum of the semiquinone radical, generated via nanosecond laser flash photolysis (355 nm) of a solution containing CA and acetophenone oxime in MeOH.

SCHEME 3



quinone radical (CA-H^\bullet) and the hydroxymethyl radical ($\text{CH}_2\text{OH}^\bullet$). Ground state CA is easily reduced ($E_{\text{red}} = +0.02 \text{ V}$), and ET from the hydroxymethyl radical ($E_{\text{ox}} = -0.98 \text{ V}$)²⁹ generates the CA radical anion (which reacts rapidly with MeOH to form the semiquinone radical),¹⁰ as well as the conjugate acid of formaldehyde, a strong acid. The acid generated this way can catalyze the acetal formation. This mechanism is energetically feasible,³⁰ but it ignores the involvement of TCHQ, which was shown to be an effective photocatalyst as well. This observation is better explained by the second sequence of reactions. Ionization of the hydroquinone (most likely via a photo-

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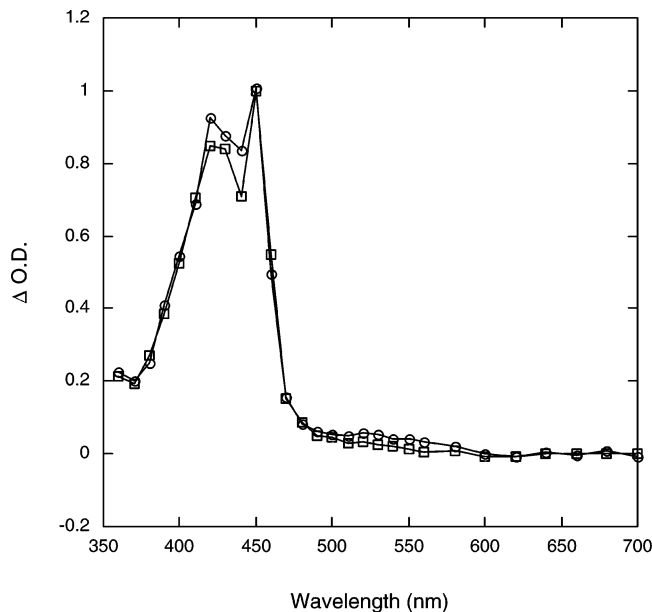


FIGURE 2. Comparison of the spectrum obtained from photolysis (355 nm) of TCHQ in MeOH (□) to that of the semiquinone radical (○). The spectra were recorded approximately 2.5 μ s after the laser pulse and are normalized.

induced electron-transfer pathway with an appropriate electron acceptor) would generate the TCHQ radical cation, a strong acid.³¹ Deprotonation of this species produces the semiquinone radical and yields the required acid for the acetalization.

The presence of formaldehyde (or the dimethylacetal) in the reaction mixture would provide evidence for this mechanism. Unfortunately, neither formaldehyde nor its dimethyl acetal can be detected by GC/FID under these conditions because of overlap with other components in the mixture. Instead, we tried a different approach and used 1-hexanol as the solvent. According to Scheme 3, 1-hexanol would react to give hexanal, which should be detectable under the conditions of the reaction. Irradiation of a mixture containing benzaldehyde and CA in 1-hexanol did indeed result in the formation of hexanal. This result is most consistent with the mechanism shown in Scheme 3.

LFP studies on TCHQ in MeOH also support the mechanism shown in Scheme 3. Photolysis of a solution containing TCHQ in MeOH results in the formation of a signal with maxima at 450 and 420 nm. Comparison of this spectrum to that of the semiquinone radical (Figure 1) shows that they are virtually identical (Figure 2), suggesting the formation of this radical species. The most

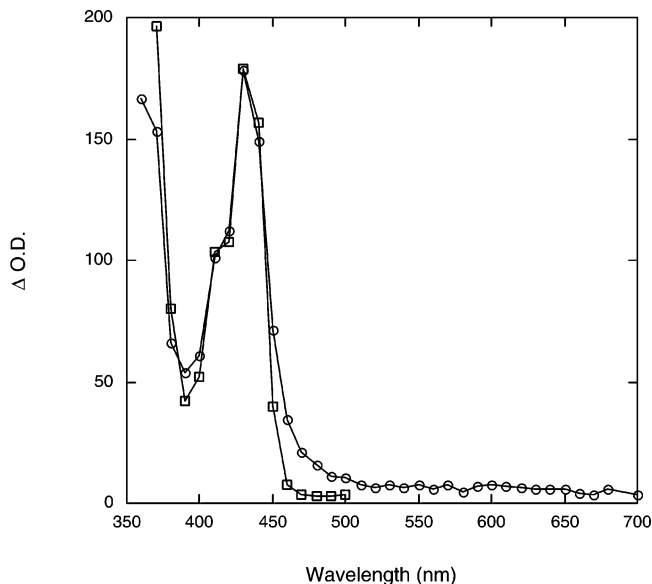


FIGURE 3. Comparison of the spectrum obtained from photolysis (355 nm) of TCHQ in MeCN (○) to that of the semiquinone radical (□). The semiquinone radical was generated via photolysis of a solution containing CA and benzyltrimethylsilane in the presence of trifluoroacetic acid. The spectra were recorded approximately 200 ns after the laser pulse.

logical explanation would be ionization of TCHQ to form the radical cation, which rapidly loses a proton to yield the (long-lived) semiquinone radical. The radical cation itself was not observed; however, this is easily explained based on the fact that phenolic radical cations react very rapidly with nucleophiles such as alcohols.⁹

A similar result was obtained by photolysis of TCHQ in acetonitrile. The observed spectrum (Figure 3) is identical to that of the semiquinone radical generated via reduction of CA in the presence of trifluoroacetic acid.¹⁰ Even in a nonnucleophilic solvent such as MeCN the deprotonation step is very fast, most likely as a result of traces of water present in the solvent.

The results described above are most consistent with a mechanism involving the two reaction sequences shown in Scheme 3 operating side-by-side. Both sequences lead to the formation of the semiquinone radical, which disproportionates to yield TCHQ, the photocatalyst, as well as CA, which can participate in a new cycle. Further studies on the scope and mechanism of these reactions, including LFP studies on the radical cations intermediates are underway.

Conclusions

Aldehydes can be conveniently converted into their dimethyl acetals via a photochemical reaction with CA in MeOH. Ketones are less reactive most likely because of steric restraints. Some ketones were found to react rapidly, but they often also produce the enol ether. Although the actual mechanism remains uncertain, the results described are most consistent with the formation of a photocatalyst (TCHQ) from CA. The actual acid is formed via ionization of TCHQ, which results in the highly acidic TCHQ radical cation. Loss of a proton to the solvent or the carbonyl species yields the semiquinone

(30) The free energy for electron transfer (ΔG_{ET}) is calculated by the following equation: $\Delta G_{ET} = E_{ox} - E_{red}$. Using the reported numbers yields $\Delta G_{ET} = -23 \text{ kcal mol}^{-1}$. Note that the reported oxidation potential for $\cdot\text{CH}_2\text{OH}$ was measured in aqueous solution. In other solvents (e.g., MeOH) this value is likely to be more positive; however, the overall reaction is still expected to be favorable. This conclusion is based on the reported oxidation potentials of $(\text{CH}_3)_2\text{C}^+\text{OH}$ in acetonitrile (-0.60 V), a 3:1 mixture of 2-propanol–acetonitrile (-1.1 V), and water (-1.30 V).²⁹ Similar trends are expected for the hydroxymethyl radical.

(31) Although the pK_a of TCHQ radical cation is not known, Bordwell and Cheng³⁰ have estimated the pK_a values of similar species; the radical cation of 3,5-dichlorophenol has a pK_a of -14 and that of 3,4,5-trichlorophenol a pK_a of -12.5 . According to these numbers, we expect the radical cation of TCHQ to be a strong enough acid to protonate a carbonyl group.

radical, which can regenerate the photocatalyst via a disproportionation reaction. The advantage of this method is that the photocatalyst is regenerated via a disproportionation reaction requiring only a catalytic amount of CA (or the hydroquinone itself). The reaction can be done at longer wavelengths, making this method attractive and potentially useful for applications requiring lower-energy radiation.

Experimental Section

Chemicals and Equipment. Methanol and acetonitrile were of spectrophotometric grade. All carbonyl compounds were of the highest purity. If necessary, they were distilled or recrystallized. All quinones were recrystallized before use. Samples were irradiated in a photochemical reactor, equipped with 16 black light phosphor bulbs ($\lambda = 350$ nm). The progress of the reactions was followed by GC/FID, and the products were identified by GC/MS. Conversion of the starting material and product yields were determined by calibrated GC/FID. Details of the experimental methods have been reported elsewhere.³²

Steady-State Photolysis Experiments. Appropriate amounts of the carbonyl compound (0.015 M) and chloranil (0.005 M) were weighed out and dissolved in 5 mL of solvent in a Pyrex tube. A small amount of the solution was removed and analyzed by GC/FID (three times). The remaining (air-

saturated) solution was irradiated in the Rayonet photochemical reactor for 30 min. Afterward, the solution was analyzed by GC/FID (three times), and the products were identified by GC/MS. Conversion of the starting material and product yields were determined by calibrated GC/FID. The photolysis of benzaldehyde and CA in MeOH under argon resulted in a similar conversion and product yield.

Laser Flash Photolysis Experiments. The apparatus used for the laser flash photolysis (LFP) experiments was of standard design,³³ and the details have been described elsewhere.³⁴ Spectra were obtained by flash photolysis (355 nm, 10 Hz, 0.5–2 mJ/pulse; 4 ns pulse width) of argon-saturated solutions (3 mL) in a glass cuvette containing the compound of interest (OD ca. 0.5–1).

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