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Flash Photolysis/HPLC Applications. 2. Direct Photolysis vs Hydrogen Peroxide Mediated Photodegradation of 4-Chlorophenol As Studied by a Flash Photolysis/HPLC Technique

Ewa Lipczynska-Kochany[†] and James R. Bolton*

Photochemistry Unit, Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

■ A method involving UV flash photolysis followed shortly by HPLC analysis of products has been applied to the study of the partial photooxidation of 4-chlorophenol (I). In this study we have compared the distribution of photoproducts obtained under conditions of hydrogen peroxide mediation with our earlier reported work on the direct photolysis of I. There it was found that the photolysis of I, stimulated by single flashes, yields quantitative amounts of p-benzoquinone (II) as the *only* primary photoproduct. When the concentration of H_2O_2 is increased to greater than 20 times that of I, the photolysis products change over to a different set. Now the major product is 4-chlorocatechol (VI) with smaller amounts of hydroquinone (IV) and 1,2,4-trihydroxybenzene (V). When several flashes are applied, IV and V become the most significant products; however, the overall yield of products IV–VI decreases, indicating that further oxidative degradation of the reaction mixture is occurring.

Introduction

Although a number of water purification techniques are available, the oxidation of aqueous organic pollutants is an attractive method because of its high efficiency and simplicity (2, 3). The oxidation products are usually low molecular weight oxygenated compounds that are easily biodegradable. In the past decade or so, the potential use of the photooxidation of organic pollutants in the presence of H_2O_2 has aroused the interest of environmental chemists (2–19).

Chlorophenols are very common pollutants, partly because of their importance in the production of fungicides and herbicides. They are also present in effluents from pulp mills. A number of experiments have been reported on the photodecomposition of some chlorophenols in the presence of hydrogen peroxide (7, 9, 15, 16, 18, 20). However, some of the data reported are questionable and inconclusive. For example, Yasuhara et al. (8) reported that high concentrations of H_2O_2 are required to decompose 2-chlorophenol, whereas Moza et al. (17) had a different opinion. Also, Draper and Crosby (10) have shown that the sunlight-induced photooxidation of many pesticides is efficient in very dilute solutions of H_2O_2. The experiments of Moza et al. (17) must be questioned as to their practical application because they were conducted

in solutions bubbled with nitrogen. They reported that catechol and 2-chlorohydroquinone are the final products of the photooxidation of 2-chlorophenol, while Omura and Matsuura (21) observed that catechol is oxidized to pyrogallol and 1,2,4-trihydroxybenzene under analogous conditions.

In view of the confusing and incomplete picture concerning the photolysis of chlorophenols in model and natural systems, we have undertaken a detailed study of the sequence of products formed in both direct photolysis and photolysis mediated by hydrogen peroxide. So far, very little is known about the mechanism of the hydrogen peroxide mediated photolysis of chlorophenols. For example, the photolysis of 2,4,6-trichlorophenol in the presence of hydrogen peroxide leads to the formation of several intermediates, as recently detected by Sundstrom et al. (19) using HPLC and GC/MS methods, but only one of intermediates, 2-chlorophenol, was identified.

The conventional methods for the study of photochemical reactions in solution usually involve irradiation of the solution with a steady-state UV light source for an extended period of time, followed by analysis using an appropriate analytical method. One of the problems with these methods is that, for reactions which may involve many photochemical steps, photolysis of intermediate products makes the analysis of reaction intermediates difficult, particularly at the low concentrations characteristic of environmental conditions. On the other hand, the use of higher concentrations (to achieve significant yield of products at low conversion fractions) leads to bimolecular coupling reactions that are not relevant to environmental conditions.

To address these problems we have developed a method utilizing the technique of flash photolysis; however, instead of using the conventional configuration where subsequent reactions are followed by detecting the optical absorption of transients, we have employed HPLC detection to detect and identify moderately lived intermediates. With this approach, we can obtain a significant fraction of conversion with a single flash and thus avoid the possibility of photolysis of intermediates. Also, by using multiple flashes, we can follow the sequence of intermediates in the reaction. This technique is limited to the detection of intermediates with lifetimes greater than ~15 min, i.e., the time required to complete an HPLC run.

We have used 4-chlorophenol (I) as a model compound for testing the method, since the photoreaction of this

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[†] On leave from Warsaw Technical University, Warsaw, Poland.

compound has been studied by Boule et al. (23), using a conventional approach, and found to be nonspecific, giving a mixture of products. In earlier papers (1, 22), we applied the method to an analysis of the reaction sequence in the direct UV photolysis of I. Since these investigations gave promising results, we decided to extend the method to the hydrogen peroxide mediated photodegradation of I, a reaction of considerable interest in pollutant removal systems utilizing UV light.

Experimental Section

Chemicals. 4-Chlorophenol, hydroquinone, and 1,2,3-trihydroxybenzene were used as received from Aldrich Chemical Inc. Methanol and acetonitrile (for liquid chromatography) were from Omnisolv. Other chemicals were from BDH.

Methods and Equipment. Samples were irradiated using a FP 1000 flash photolysis system, Photochemical Research Associates Inc. The UV light was provided by two 100-J xenon flash lamps (Model FX 141C-3.5, EG & G Inc., Electro-Optics Division) located on either side of the sample chamber. The flash duration was ~10 μs (fwhm) at 49-J discharge (7-kV and 2-μF capacitor), but the lamp profile showed a long tail extending to ~30 μs. Repetitive flashes were ~2 s apart.

High-performance liquid chromatography (HPLC) was performed with a Waters Model 501 HPLC apparatus, equipped with a μ-Bondapak C_{18} column, Waters Model 441 absorbance detector set at λ = 254 nm, Waters Lambda-Max Model 481 LC spectrophotometer set at λ = 280 nm, and a Fisher Recordall Series 5000 dual-channel recorder.

Irradiations were performed using a quartz cell (length 10.0 cm, diameter 1.0 cm). Progress of the photochemical degradation of 4-chlorophenol (I) in undegassed water containing H_2O_2 (0.070 M) was observed, with the concentration of I kept at 6.4×10^{-4} M while the number of flashes (45 J) varied. The pH of the unbuffered solution before flashing was 4.7. The effect of the concentration of H_2O_2 on the degradation of I was determined by varying the H_2O_2 concentration between 4×10^{-4} and 0.1 M, keeping the electrical energy input into the flash lamps constant, 2×45 J.

All flashed solutions were analyzed by the HPLC method within 2 min after the irradiation. Products were identified by comparison of their retention times with those of authentic samples. A mixture of acetonitrile/water (20/80), acidified to pH ~4.5 with orthophosphoric acid, was used as an eluent. Details of the analysis have been reported elsewhere (1).

Results and Discussion

In our earlier reports (1, 22) we examined the photolysis of I under direct photolytic conditions. The analysis of an undegassed aqueous solution of I following a single flash indicated that p-benzoquinone (II) is the only primary photoproduct, since II is formed in almost stoichiometric amounts (>98%) from I.

In our present study, involving the influence of the presence of hydrogen peroxide, we have carried out two sets of experiments, one in which the number of flashes was changed and the other in which the ratio of H_2O_2 to I was varied. In the first series, solutions of I (6.4×10^{-4} M), containing 0.070 M H_2O_2, were subjected to several single flashes (45 J) and then analyzed by HPLC. Figure 1 shows the depletion of I and the formation of the photoproducts as a function of the number of flashes. It is clear that with a single flash 4-chlorocatechol (VI) is the
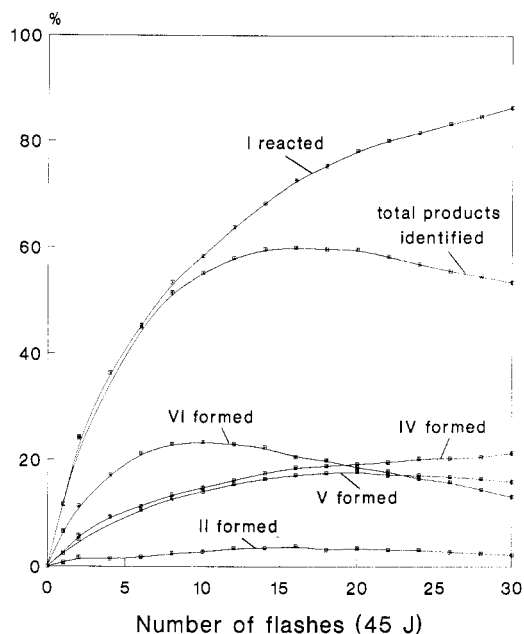

Figure 1. Mole fractions (%) of reactant and products present in an aqueous solution of I subjected to a number of flashes (45 J). Detection was by HPLC analysis. Solution composition was initially 6.4×10^{-4} M in I and 0.070 M in H_2O_2. Repeat experiments indicated that the reproducibility of a given data point is ±3% absolute.
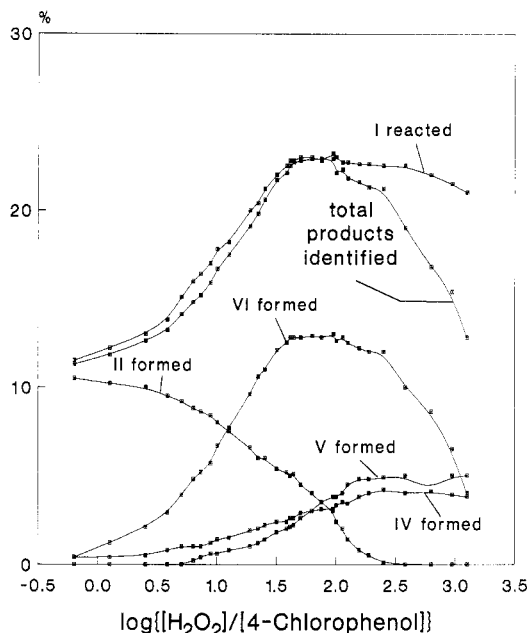

Figure 2. Mole fractions (%) of reactant and products present in an aqueous solution of I (held at an initial concentration of 9.6×10^{-4} M) as a function of log $[H_2O_2]/[4$-chlorophenol]. Each solution was subjected to two 45-J flashes.

major product, with smaller amounts of hydroquinone (IV) and 1,2,4-trihydroxybenzene (V). After 10 flashes, IV and V become the major products. We also note that for a larger number of flashes, the total amount of the identified products II and IV–VI is significantly less that the amount of I reacted. This indicates that further degradation reactions are occurring under the conditions of our experiments.

In the second set of experiments, the concentration of hydrogen peroxide was varied, keeping the concentration of I at 9.6×10^{-4} M. Figure 2 shows a plot of the product yields as a function of the logarithm of the concentration ratio. At concentration ratios between 0.6 and 20 (log

Scheme I
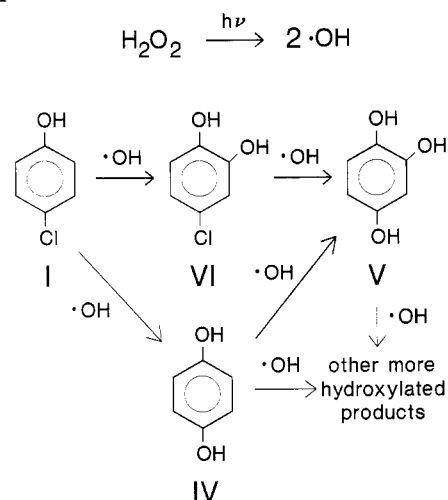
[H_2O_2]/[4-chlorophenol] = -0.2 to 1.3), the amount of II decreases while the amounts of IV and V increase significantly. This shows a clear changeover of products from those found in direct photolysis to those found in the hydrogen peroxide mediated photolysis. At concentration ratios between 20 and 1000, the amount of 4-chlorocatechol (VI) formed drops significantly with an increase in the concentrations of IV and V observed (Figure 2). At even higher ratios, the amount of I reacted does not change significantly; however, the distribution of products changes markedly. This probably is a consequence of the fact that at higher H_2O_2 concentrations the UV light is absorbed in a thin film near the front surface and hence the local concentration of •OH radicals in that reaction zone will be much higher. I is distributed uniformly throughout the cell, and so the fraction of I reacted does not increase significantly; however, photoproducts are concentrated in the reaction zone near the front surface where the highest concentration of •OH radicals is present and so they react further.

It has been known for a long time that hydrogen peroxide photolyses to produce •OH radicals. This reaction has been studied in detail by EPR spectroscopy using a spin-trapping technique (24, 25). It is well-known that •OH radicals react with aromatic compounds by adding to the ring to produce hydroxylated products. Thus, the observation that VI is the major product after a single flash is quite understandable. Some •OH radicals also displace chlorine atoms in I since IV and V are significant products. The proposed reaction sequence for the hydroxylation of I is shown in Scheme I.

Conclusions

In our extension of our new method of flash photolysis/HPLC to the hydrogen peroxide mediated photodegradation of I, we come to the following conclusions:

1. As the ratio [H_2O_2]/[I] increases, the photoreaction mechanism changes from direct photolysis (where II is the major direct photoproduct) to H_2O_2-mediated photolysis (where VI is the major photoproduct).

2. Direct photolysis of I leads primarily to non-chlorinated benzenoid compounds with little further reaction; whereas, H_2O_2-mediated photolysis results in hydroxylation reactions to produce less stable intermediates, which do proceed in further degradative processes.

From our observations we suggest that the H_2O_2-mediated photolysis process, rather than direct photolysis, should be the preferred approach in strategies to remove pollutants from natural and industrial waters.

The technique used during this work is only able to detect compounds and intermediates stable enough to be detected by HPLC. In another investigation, using EPR spectroscopy, we are examining the primary processes involved in the hydrogen peroxide mediated photodegradation of aromatic pollutants (26–28). The results will be published in the near future.

Finally, we conclude that the new technique of flash photolysis/HPLC is very effective in elucidating the detailed reaction sequence of aqueous photochemical reactions of environmental interest. We intend to apply the method to the study of other chlorophenols and chloroorganic pollutants.

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Mechanism of Photodegradation of Aqueous Organic Pollutants. 2. Measurement of the Primary Rate Constants for Reaction of •OH Radicals with Benzene and Some Halobenzenes Using an EPR Spin-Trapping Method following the Photolysis of H₂O₂

Jan Kochany[†] and James R. Bolton*

Photochemistry Unit, Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

■ The technique of spin trapping, with EPR detection of spin adducts, has been applied to the study of the photodegradation of benzene, chlorobenzene, bromobenzene, iodobenzene, o-dichlorobenzene, m-dichlorobenzene, and p-dichlorobenzene sensitized by the photolysis of H_2O_2 in aqueous solution. By employing a competition kinetic scheme and relative initial slopes or signal amplitudes, plus published rate constants for the reaction of •OH radicals with the spin trap (DMPO), it has been possible to obtain rate constants for the reaction of •OH radicals with benzene and its halo derivatives. Rate constants obtained by this method at neutral and acidic solutions are similar to published methods using pulse radiolysis, where available. Significant differences were found for measurements carried out in basic solutions. The rate constants do not vary much among the halobenzene derivatives studied, and an average rate constant of $\sim 5.0 \times 10^9$ M^{-1} s^{-1} could be used for any of these compounds.

Introduction

Many organic chemicals discharged into the aquatic environment are not only toxic but also only partly biodegradable, in that they are not easily removed in biological wastewater treatment plants. That is why there is a need to develop effective methods for the degradation of organic pollutants, either to less harmful compounds or to their complete mineralization.

During the last few years a series of new methods for water and wastewater purification, called advanced oxidation processes, have received increasing attention. They rely mainly on the use of short-lived oxidative species (often hydroxyl radicals) generated by photolysis (*1–6*) and radiolysis (*7–10*). The main advantages of these methods are high rates of pollutant oxidation, flexibility concerning water quality variations, and small dimensions of the equipment (*11–13*). The main disadvantages are high operating costs and special safety requirements because of the use of very reactive chemicals (ozone, hydrogen peroxide, etc.) and high-energy sources (UV lamps, electron beams, radioactive sources).

In spite of several reviews (*14–17*) reporting degradation rates for a variety of pollutants, very little is known about the detailed mechanism of oxidation of organic pollutants in water, except that hydroxyl radicals are important intermediates. Understanding the mechanism is very important if the optimization of these processes is to be achieved.

The aim of our investigations is to contribute to an understanding of the photodegradation mechanisms of organic pollutants in homogeneous systems. We have focused our interests on the photolysis of hydrogen peroxide in aqueous solution as a source of hydroxyl radicals. This reaction is known to produce hydroxyl radicals cleanly (*18*), and it is practical, since H_2O_2 is used in commercially produced equipment for water and wastewater purification (*10–13*).

Most available data (*19*) concerning the rate constants of the reactions of hydroxyl radicals in water toward different organic compounds have been obtained from systems where the hydroxyl radicals were generated by pulse radiolysis. The photolysis of H_2O_2 is an alternative source of •OH radicals, and some rate constants (*20*) have been obtained using this source. However, here one must take account of the possibility of direct photolysis of the organic substance, a process not important in radiolysis. It follows that one may encounter differences in the apparent rate constants of •OH reacting with the same compound obtained using either pulse radiolysis or photolysis.

We have developed a reliable procedure for determining the primary rate constants for the attack of •OH radicals on pollutant molecules using a competition method based on the technique of spin trapping (*21*) with detection by electron paramagnetic resonance (EPR) spectroscopy. This method uses a *spin trap* molecule, e.g., 5,5′-dimethylpyrroline *N*-oxide (DMPO), that reacts rapidly with a variety of reactive radicals, such as •OH and HO₂•, to produce relatively long-lived *spin-adduct* nitroxide radicals that can be detected readily by EPR. Although this method is relative, we have validated it by reproducing several published rate constants that have been determined previously using pulse radiolysis (*21*). In this paper we apply our method to the determination of primary •OH radical rate constants for benzene and some of its halo derivatives.

Experimental Section

The spin trap used was 5,5′-dimethylpyrroline *N*-oxide (DMPO), which reacts with free radicals, such as •OH (*22*), to form moderately stable nitroxides (spin adducts). This

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†On leave from the Institute for Environmental Protection, Warsaw, Poland.