FT-EPR Study of the Photolysis of 4-Chlorophenol

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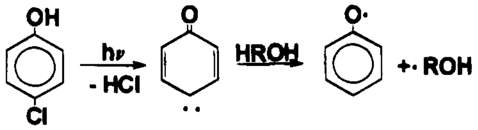
Fourier transform electron paramagnetic resonance (FT-EPR) has been used to identify the transient free radicals formed in the photolysis of 4-chlorophenol (4CP) dissolved in alcohols and to get information on their precursor from CIDEP effects. It is found that photolysis of 4-diazo-2,5-cyclohexadienone in 2-propanol produces the same FT-EPR spectrum as that produced by photolysis of 4CP. The results lend strong support to the recent proposal[1] that the photochemistry of 4CP in aqueous and alcohol solutions involves formation of the carbene 4-oxocyclohexa-2,5-dienylidene.

A number of publications have been concerned with the photolysis of 4-chlorophenol (4CP).[1–4] The interest in the photochemistry of 4CP, and halogenated phenols in general, stems from efforts to develop a method for the photodegradation of these important pollutants. The primary products formed upon photolysis of 4CP depend strongly on reaction conditions.[1–4] For instance, in oxygenated aqueous solution the reaction produces benzoquinone, whereas hydroquinone is the major product under anaerobic conditions. In the presence of hydrogen donors or in alcohol solution phenol is formed.

The mechanism that accounts for the formation of these products has been a point of discussion for some time. On the basis of data from an EPR study using the spin-trapping technique, Lipczynska-Kochany et al.[4] propose that excitation of 4CP in aqueous solution can involve two distinct initial steps giving free radicals: one producing the hydroxyphenyl radical generated by dechlorination and the other producing the 4-chlorophenoxy radical by photoionization of 4CP. Very recently, results of a detailed flash photolysis study of the photochemical reactions of 4CP under a variety of conditions led to the formulation of a new mechanistic interpretation.[1] The study provides evidence that photoexcitation of 4CP in aqueous solution produces the 4-oxocyclohexa-2,5-dienylidene (carbene) as the first detectable transient reaction product. Reactions of the (triplet state) carbene account for the stable reaction products found under different conditions. It is of special note that quenching by alcohols of the transient absorption assigned to the carbene is accompanied by a growing in of the absorption spectrum of the phenoxyl radical. This is attributed to the hydrogen abstraction reaction:[1]



The assignment of the initial transient absorption spectrum to the carbene is supported by convincing evidence.[1] Even so, the identification is not unequivocal, and it would be useful to have additional spectroscopic evidence regarding the course of the reaction. FT-EPR, by identifying the transient free radicals formed in the photolysis of 4CP and the spin state of their precursor, provides strong support for the novel reaction scheme.

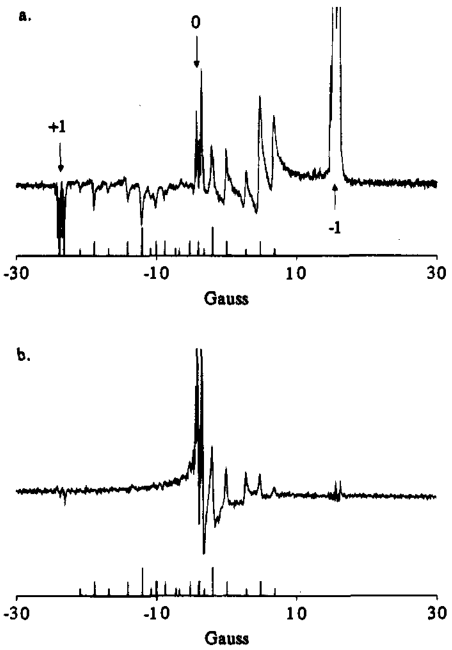


Figure 1. FT-EPR spectra from (a) 4CP (0.1 M) in 2-propanol excited with 308 nm laser light (groups of lines from the 2-propanoyl radical are marked by +1, 0, and −1) and (b) 4-diazo-2,5-cyclohexadienone (10^{-2} M) in 2-propanol excited with 355 nm laser light. Delay between laser pulse and microwave pulse: 0.5 μs. Because of the large spectral width, FIDs for spectrum a were recorded with three field settings separated by 2 mT. The displayed spectrum is assembled from the three measurements.[5b] Spectrum b was recorded with a single field setting and shows strong attenuation of intensies at low- and high-field sides because of bandwidth limitations. Predicted line positions for the phenoxyl radical spectrum are given by the stick spectra.

Figure 1a depicts the FT-EPR spectrum produced by pulsed-laser (308 nm, ~30 mJ) excitation of 4CP (~0.1 M) in 2-propanol.[5] It shows three groups of lines from the center of the spectrum given by the 2-propanoyl radical ($g = 2.003\,17$, $a(6H) = 1.97$ mT, $a(1H) = 0.07$ mT[6]). In addition, a series of resonances that match the positions predicted for the phenoxyl radical ($g = 2.0053$, $a(2H) = 0.7$ mT, $a(2H) = 0.2$ mT, $a(1H) = 1.0$ mT[7]), marked by the stick spectrum, is observed.

Resonances on the low-field side of the spectrum are in emission, those on the high-field side in absorption due to radical pair mechanism (RPM) CIDEP.[8] The CIDEP pattern establishes that the free radicals are produced in a reaction step that produces the triplet state [phenoxyl• •2-propanoyl] radical pair.

FT-EPR spectra do not show evidence for the formation of the primary free radicals that play a role in the reaction scheme proposed by Lipczynska-Kochany et al.[4] In terms of free radical identities and CIDEP pattern, the results indicate that excitation of 4CP leads to formation of a triplet state species which in a subsequent step abstracts a hydrogen atom from 2-propanol to

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give the two radicals detected. It can be concluded that the EPR data fit the reaction mechanism advanced by Grabner et al.[1]

With EPR one does not expect to observe the spectrum from the carbene because of line broadening caused by interaction between the unpaired electrons in the triplet. However, indirect evidence for the formation of the carbene upon photolysis of 4CP is provided by the FT-EPR spectrum given upon photolysis of a solution of 4-diazo-2,5-cyclohexadienone[10] in 2-propanol. It is known that this diazide gives the triplet carbene.[11] Therefore, photolysis should generate a spectrum that is identical to that from 4CP in 2-propanol if the proposed mechanism is correct. As is shown in Figure 1b, excitation of quinone diazide (10^{-2} M) in 2-propanol with 355 nm light of a Nd:YAG laser indeed leads to the formation of the phenoxyl,and 2-propanoyl radicals. To the extent that the hyperfine components can be discerned, the spectrum displays a RPM CIDEP pattern similar to that given by 4CP in 2-propanol.

Concluding, the FT-EPR study provides strong support for the proposal[1] that photoexcitation of 4CP in aqueous and alcohol solutions leads to formation of a triplet state carbene.

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