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Phototransformation of chlorohydroquinone in aqueous solution

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Abstract

The photolysis of chlorohydroquinone (QH_2Cl) in aerated or degassed solution leads to the formation of hydroquinone (QH_2) and chlorobenzoquinone (QCl) as the main photoproducts. In the initial stage of the reaction, they are formed at the same rate and account for about 80% of QH_2Cl converted. The formation of benzoquinone (Q) and chlorohydroxybenzoquinone (QOHCl) was also observed and evaluated. The conversion into Q is favoured by dilution. QOHCl results from a secondary reaction. A radical mechanism involving semiquinone and chlorosemiquinone radicals is proposed, since transients absorbing in the range 400–450 nm were detected by flash photolysis. The UV spectrum of $QCl^{\cdot -}$ can be observed without irradiation in a basic solution of QH_2Cl. It is red shifted by about 7 nm compared with the spectrum of $Q^{\cdot -}$. The formation of QH_2, previously observed in the induced photo-oxidation of 2-chlorophenol and 3-chlorophenol, is attributed to the photolysis of QH_2Cl formed in the initial stage of the reaction.

Keywords: Phototransformation; Chlorohydroquinone

1. Introduction

Chlorophenols are involved in the synthesis and degradation of many pesticides. They are water soluble and can pollute the aquatic environment. Phototransformation contributes to their elimination and there is great interest in the mechanisms of the reactions involved.

Chlorohydroquinone is one of the main products formed in the photocatalytic degradation of 2-chlorophenol, 3-chlorophenol, 1,2- and 1,3-dichlorobenzene [1–3]. It also appears in the photo-oxidation of 2-chlorophenol and 3-chlorophenol induced by the excitation of nitrate ions [4]. More surprisingly, the formation of hydroquinone and benzoquinone is also detected in the latter reaction. This reaction has ecological importance since hydroquinone is more toxic than monochlorophenols. It can be suggested that hydroquinone results from the photolysis of chlorohydroquinone, but such a reduction in strong oxidizing conditions has not been proven experimentally. The aim of this work is to analyse the photoproducts of chlorohydroquinone and to propose a mechanism for the transformation.

2. Experimental details

Chlorohydroquinone (QH_2Cl) (Fluka pract.) contains hydroquinone (QH_2) as the main impurity (about 5%). It was recrystallized twice in hexane. The final product contained small amounts of QH_2 (less than 1%) and chlorobenzoquinone (QCl) (less than 0.5%). QH_2 (99.5%) and benzoquinone (Q) (for synthesis) obtained from Merck were used for analytical purposes. Q was sublimated before use to remove QH_2 contained as an impurity. QCl was obtained by oxidizing QH_2Cl with chromic acid according to Ref. [5]. Its molar extinction coefficient at $\lambda = 254$ nm was evaluated to be 14 700 $M^{-1}\ cm^{-1}$.

Solutions were irradiated in a monochromatic parallel beam at 296 nm with a Bausch and Lomb monochromator equipped with a high-pressure mercury lamp. Irradiated solutions were analysed by high performance liquid chromatography (HPLC) with a reverse phase C_{18} column (250 mm × 4 mm) and UV detection. The UV spectra of the solutions were recorded on a Cary 3 (Varian) spectrometer. A Nortech FPX-1 apparatus was used for microsecond flash photolysis.

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3. Results

The first pK_a value of QH_2Cl was evaluated to be about 8.8. This value is not very accurate because of the existence of a second pK_a value and the oxidizability of the anionic form. In unbuffered or acidic solution kept in the dark no change was observed after several days. The maximum of the UV band of the molecular form is located at 293 nm, $\epsilon = 3300\ M^{-1}\ cm^{-1}$.

When unbuffered solutions (10^{-3} M; air-saturated, oxygen-saturated or argon-purged) were irradiated at 296 nm, a new band located at 260 nm appeared in the UV spectrum. The presence of oxygen has only a small influence on this process. The main products detected by HPLC are QH_2, QCl and Q. Another product was identified as chlorohydroxybenzoquinone (QOHCl) for two reasons: (a) it is dissociated in unbuffered solution and the UV spectrum of its anionic form ($\lambda_{max} = 510$ nm) is similar and red shifted relative to the UV spectrum of hydroxybenzoquinone (QOH) ($\lambda_{max} = 485$ nm); (b) the same product is formed by photolysis of QCl and accounts for about 50% of the conversion; the other product is QH_2Cl. This reaction

$$2QCl \xrightarrow[H_2O]{h\nu} QH_2Cl + QOHCl$$

is very similar to the reaction observed with Q [6]

$$2Q \xrightarrow[H_2O]{h\nu} QH_2 + QOH$$

In the photolysis of QH_2Cl, QH_2 and QCl are initially formed at the same rate and account for about 80% of the QH_2Cl converted. Q and QOHCl are minor products, but their formation is self-accelerated (Fig. 1). Similar results were obtained in oxygen-saturated solution or after deoxygenation by argon bubbling. The quantum yield was evaluated to be 0.11 ± 0.02 independent of the oxygen concentration.

The mass balance was somewhat different in more dilute solutions (5×10^{-5} M). The initial yields of the photoproducts were evaluated to be 36% for QH_2, 36% for QCl, 21% for Q and 5% for QOHCl in aerated and deoxygenated solutions. It appears that the formation of Q is enhanced by QH_2Cl dilution.

Flash photolysis was used to detect the intermediate species involved in the reaction. A transient absorbing between 400 and 440 nm was observed. Its decay obeys second-order kinetics. Its spectrum (Fig. 2) is similar to the UV spectrum of the semiquinone anion $Q^{\cdot -}$. It is comparable with the UV spectrum obtained for QH_2 or QH_2Cl in basic solution. It is well known that the radical anion $Q^{\cdot -}$ can be observed in an aerated or deoxygenated mixture of $Q + QH_2$ at pH > 7. Its formation is attributed to the equilibrium

$$Q^{2-} + Q \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2Q^{\cdot -}$$

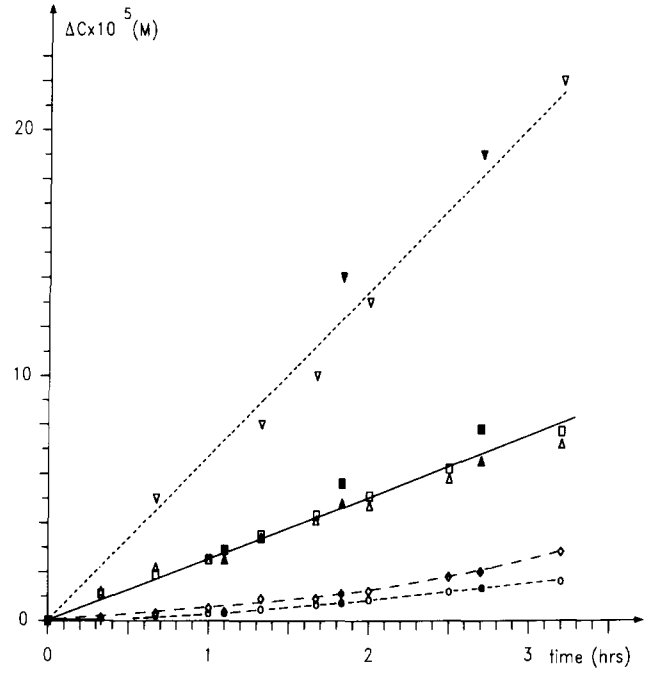


Fig. 1. Kinetics of phototransformation of QH_2Cl in unbuffered solution (10^{-3} M) irradiated at 296 nm: ▽ ▲, QH_2Cl conversion; □, ■, QH_2; △, ▲, QCl; ◇, ◆, Q; ○, ●, QOHCl; open symbols, air-saturated solution; filled symbols, deoxygenated solution.

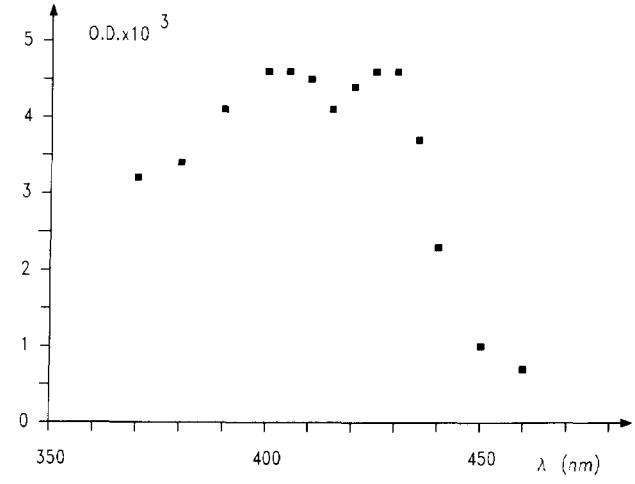


Fig. 2. Absorption spectrum of the transient observed by flash photolysis in an air-saturated solution of QH_2Cl (6.6×10^{-5} M).

where $k_1 = 2.6 \times 10^8\ M^{-1}\ s^{-1}$ and $k_2 = 7 \times 10^7\ M^{-1}\ s^{-1}$ [7].

A similar spectrum can be obtained from a solution of QH_2Cl, but the maxima are red shifted by about 7 nm (Fig. 3). This spectrum, observed for more than 1 h in a partly deoxygenated solution, can be attributed to the chlorosemiquinone anion $QCl^{\cdot -}$ resulting from the equilibrium

$$QCl^{2-} + QCl \rightleftharpoons 2QCl^{\cdot -}$$

The lifetime of the transient is shorter in air-saturated solution.

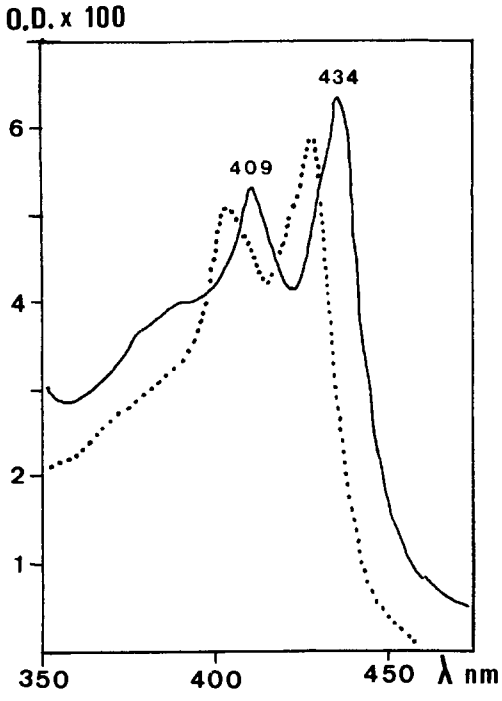


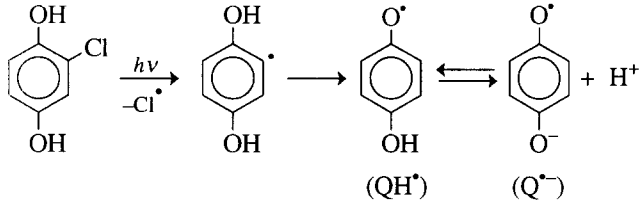
Fig. 3. Full line: absorption spectrum attributed to the chlorosemiquinone radical anion $QCl^{\cdot -}$ observed in a solution of QH_2Cl (3×10^{-4} M) at low oxygen concentration, pH 8.1. Dotted line: spectrum of $Q^{\cdot -}$ obtained from $Q+QH_2$ in basic solution, for comparison.

The resolution of the UV spectrum obtained on flash photolysis of QH_2Cl is not sufficient to discriminate in favour of $Q^{\cdot -}$ or $QCl^{\cdot -}$. It is probable that both species are formed.

4. Discussion and mechanism

Heterolytic scission of the C–Cl bond is ruled out for the first step of the reaction, because this process cannot explain the formation of QCl and it is expected to lead to the specific formation of Q after deprotonation of the organic cation. Besides heterolysis does not fit with the observed formation of the semiquinone radical anion.

Homolytic scission with the formation of $Cl^{\cdot}$ and the dihydroxyphenyl radical is suggested. The latter is expected to rearrange into the semiquinone radical



The formation of QCl is attributed to the oxidation of QH_2Cl by $Cl^{\cdot}$, followed by the oxidation of the intermediate radical formed

$$QH_2Cl + Cl^{\cdot} \xrightarrow[-HCl]{} QHCl^{\cdot} \rightleftharpoons QCl^{\cdot -} + H^+$$

$$Q^{\cdot -}\ (\text{or } QH^{\cdot}) + QCl^{\cdot -}\ (\text{or } QHCl^{\cdot}) \xrightarrow{H^+} QH_2 + QCl$$

Both the radicals $QH^{\cdot}$ and $QHCl^{\cdot}$ and the radical anions $Q^{\cdot -}$ and $QCl^{\cdot -}$ can disproportionate or react together. The formation of QH_2 and QCl with the same yield is explained when the latter reaction is the main pathway at low conversion.

The disproportionation of $QCl^{\cdot -}$ and $Q^{\cdot -}$ should lead to equivalent yields of Q, QH_2 and QCl, which was not observed in most cases.

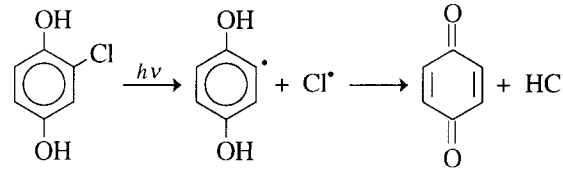
The self-accelerated formation of Q in the photolysis of QH_2Cl (10^{-3} M) is attributed to the reaction of $Cl^{\cdot}$ with QH_2 formed in the initial stage of the reaction

$$Cl^{\cdot} + QH_2 \longrightarrow HCl + QH^{\cdot} \longrightarrow Q + QH_2$$

This reaction was confirmed by the following experiment: it was observed that, after one single flash, the formation of Q in an equimolar mixture of QH_2Cl and QH_2 was significantly higher than in the separate photolysis of QH_2 and QH_2Cl at the same concentration.

The proposed mechanism is consistent with the observed second-order disappearance of radical anions in flash photolysis.

The fact that the formation of Q is enhanced in dilute solution may be explained by an oxidoreduction between the two radicals formed in the initial photochemical scission



This reaction becomes negligible with increasing QH_2Cl concentration because of the competitive oxidation of QH_2Cl by $Cl^{\cdot}$.

The formation of QOHCl results from the photolysis of QCl according to the mechanism previously proposed for the transformation of unchlorinated benzoquinone [6].

5. Conclusions

The photolysis of QH_2Cl in aqueous unbuffered solution (10^{-3} M) yields QH_2 and QCl as the main products. The formation of Q and QOHCl was also detected. These reactions are not influenced by the

presence of oxygen. The formation of Q is favoured by the initial dilution of QH_2Cl.

The radical anion $QCl^{\cdot -}$ can be easily observed in a basic solution of QH_2Cl. Its absorption maxima are located at 434 and 409 nm.

The phototransformation of QH_2Cl is explained by a radical mechanism involving both radical anions $Q^{\cdot -}$ and $QCl^{\cdot -}$ or their protonated forms.

The formation of QH_2 as one of the main photoproducts explains why QH_2 was previously detected in the induced photo-oxidation of 2-chlorophenol and 3-chlorophenol since QH_2Cl is formed in both reactions.

References

[1] T. Sehili, P. Boule and J. Lemaire, *J. Photochem. Photobiol. A: Chem., 50* (1989) 103.
[2] T. Sehili, P. Boule and J. Lemaire, *J. Photochem. Photobiol. A: Chem., 50* (1989) 117.
[3] J.-C. D'Oliveira, G. Al-Sayyed and P. Pichat, *Environ. Sci. Technol., 24* (1990) 990.
[4] G. Schedel, D. Lenoir and P. Boule, *Chemosphere, 22* (1991) 1063.
[5] S. Levy and G. Schultz, *Liebigs Ann. Chem., 210* (1881) 133.
[6] A. Rossi, G. Guyot and P. Boule, *C.R. Acad. Sci., Ser. B, 303* (1986) 1179.
[7] H. Diebler, M. Eigen and P. Matthies, *Z. Naturforsch., Teil B, 16* (1961) 629.