Steady State Photolysis and Product Analysis of 4-Chloroanisole in Aqueous Solutions

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Aqueous solutions of 4-Chloroanisole (4ClA) of various concentrations saturated with Ar, N_2O, air, and O_2 were photolyzed under steady state conditions using uv-light of 228.8 and 253.7 nm. The reaction products (4-methoxyphenol, 4-chlorophenol, anisole and hydroquinone) were detected by HPLC. Mechanisms which account for these photoproducts are suggested.

1. Introduction

As a consequence of the rapid development of various industries during the last decades and the worldwide application of fertilizers, pesticides etc. in modern agriculture, water resources became heavily polluted. Chlorinated organic compounds are considered as dangerous water pollutants. As an alternative to electron- and γ-rays the use of uv-light has been suggested for degradation of such compounds ([1] and references therein). Further, it has been established that aqueous anisole can eject electrons its S_1 and S_2 excited states [2].

In the present work, 4-chloroanisole (4ClA) was chosen as a model substrate, and its photoinduced decomposition was studied under steady state conditions using monochromatic light of 228.8 and 253.7 nm. In order to elucidate the reactivity of the transients involved in the decomposition process of 4ClA, the solutions were saturated with different gases (Ar, N_2O, air, and O_2). Based on the analysis of final products, a possible reaction mechanism is suggested.

2. Experimental

Light Sourced and Actinometry

Two different low pressure uv-lamps served as light sources. A Hg-lamp (Osram HNS 10 W) with Vycor filter, which absorbs the 184.9 nm line, provided monochromatic uv-light of $\lambda = 253.7$ nm. Using air-free 0.5 mol dm^{-3} $ClCH_2COOH$ as actinometer (light path $d = 1$ cm) with a quantum yield $Q(Cl^-) = 0.37$ at 32 °C [3], a light intensity $I_0 = 6.5 \times 10^{17}$ $h\nu\,ml^{-1}\,min^{-1}$ was determined. Further, a Philips low pressure Cd-lamp emitting at $\lambda = 228.8$ nm was also applied. Using the same actinometer system as before, but with higher Cl-yield (0.6) [3], an intensity $I_0 = 4 \times 10^{16}$ $h\nu\,ml^{-1}\,min^{-1}$ was determined. All uv-irradiation experiments were carried out at 32 °C in a thermostated double walled irradiation vessel with quartz tubes and 4π-geometry, described previously [4].

Preparation of Solutions and Analysis

p-Chloroanisole (Aldrich 99%) was used as received and dissolved in triply distilled water which had been saturated with the corresponding gas before irradiation with uv-light.

The Cl^- yield was used as indicator for the degree of substrate decomposition. The Cl^- determination was performed according to the method by Florence [5].

Aqueous solutions of 4ClA were irradiated under steady state conditions at $\lambda = 253.7$ and 228.8 nm and subsequently analysed by an HPLC chromatograph (Hewlett-Packard 1050, Sphersorb ODS2 125 nm column; eluent: $H_2O/MeOH = 50/50$ by volume). The HPLC was equipped with a multiple wavelength uv-detector. The absorption of the individual products was detected at 210, 225 and 280 nm, and their identity was confirmed by comparison with the identity chromatograms of standards.

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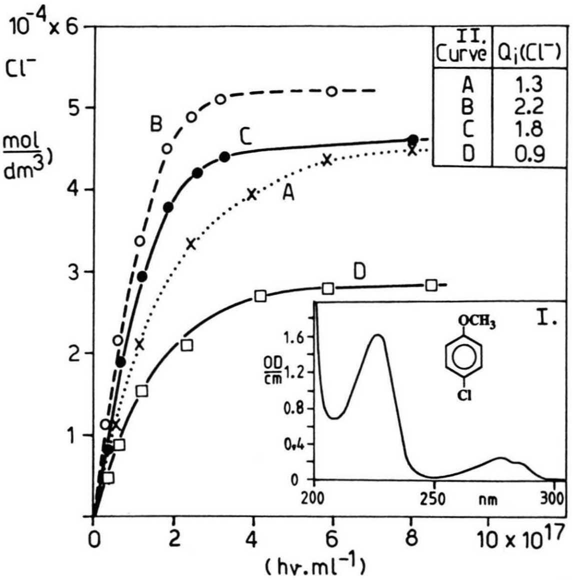


Fig. 1. Photoinduced Cl^- formation from 5.0×10^{-4} mol dm^{-3} 4ClA. (A) Airfree solution, (B) in the presence of 2.8×10^{-2} mol dm^{-3} N_2O, (C) in the presence of 0.25×10^{-3} mol dm^{-3} O_2, and (D) in the presence of 1.25×10^{-3} mol dm^{-3} O_2, as a function of the uv-dose ($\lambda = 253.7$ nm) at pH 7. *Insert I:* Absorption spectrum of 1.0×10^{-4} mol dm^{-3} 4ClA in water at pH 7. *Insert II:* Initial Cl^- yields ($Q_i(Cl^-)$).

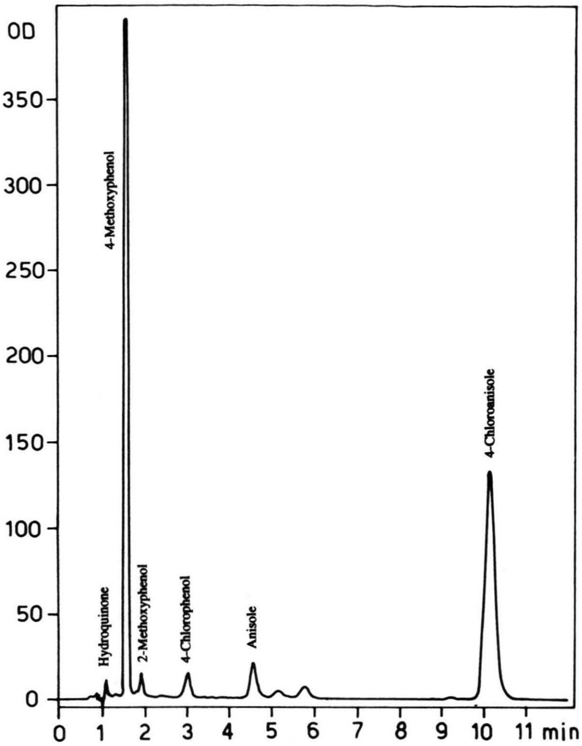


Fig. 2. HPLC separation chromatogram of the photoinduced products from 7.5×10^{-4} mol dm^{-3} 4ClA in the presence of Argon at pH 7, applied dose 5×10^{17} h ml^{-1} ($\lambda = 253.7$ nm).

3. Results

The absorption spectrum of 4ClA shows two maxima at 227 and 278 nm (Fig. 1, insert I). On absorption of light 253.7 and 228.8 nm, 4ClA is promoted to its first and second singlet states, respectively. In order to determine the influence of different reaction conditions on the reaction mechanism, solutions of various concentrations and pH under Ar, N_2O, air and O_2 were irradiated.

Figure 1 shows the Cl^- yield resulting from 4ClA as a function of adsorbed uv-dose under four different experimental conditions using light of $\lambda = 253.7$ nm. The quantum yields of photolytically formed Cl^- ions, $Q(Cl^-)$, were calculated from the linear part of the individual curves in Fig. 1. The high Q-values indicate that not only simple homolization of the C–Cl bond is taking place, but at least one additional reaction must be involved.

In all experiments, 4-methoxyphenol was found to be the major product. Anisole, chlorophenol and hydroquinone were also detected in minor quantities. A typical HPLC-chromatogram is presented in Figure 2. It might be pointed out that the product distribution strongly depends on the experimental conditions.

The pH of the solution had a relatively small influence on the product distribution. The initial quantum yields decreased slightly by changing the pH from 7 to 12 as can be seen by comparing the data of Figs. 3 and 4. This effect is explained by the lower reactivity of $O^{\cdot -}$ species in contrast to that of the OH radicals ($OH \rightleftharpoons O^{\cdot -} + H^+$, pK = 11.9).

In the presence of 2.8×10^{-2} mol dm^3 N_2O, the substrate decomposition is more efficient and the yields of the products are much higher than in the airfree solutions (Figure 5). Rather high product yields were also observed in solutions saturated with oxygen. In this case, the hydroquinone yield increases because of secondary photochemical reactions of 4ClA. Neither products resulting from ring opening-reactions nor peroxides were detected.

On irradiation with uv-light of wavelength $\lambda = 228.8$ nm, which promotes the molecule into its second singlet state, no anisole was found (Figure 6). In

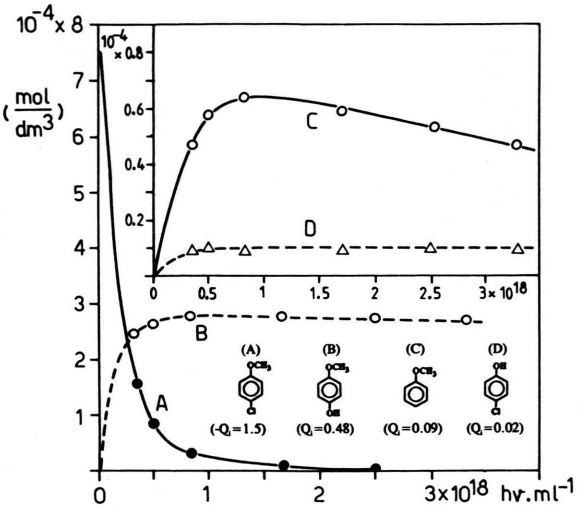


Fig. 3. Photoinduced decomposition of 7.5×10^{-4} mol dm^{-3} 4ClA (A) and formation of 4-methoxyphenol (B), anisole (C), and 4-chlorophenol (D) as a function of absorbed uv-light ($\lambda = 253.7$ nm) at pH 7 in absence of air.

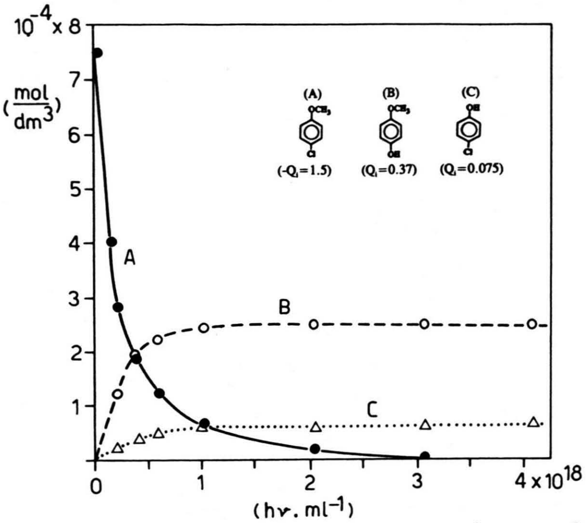


Fig. 4. Photoinduced decomposition of 7.5×10^{-4} mol dm^{-3} 4ClA (A) and formation of 4-methoxyphenol (B), and 4-chlorophenol (C) as a function of absorbed uv-light ($\lambda = 253.7$ nm) in airfree solution at pH 12.

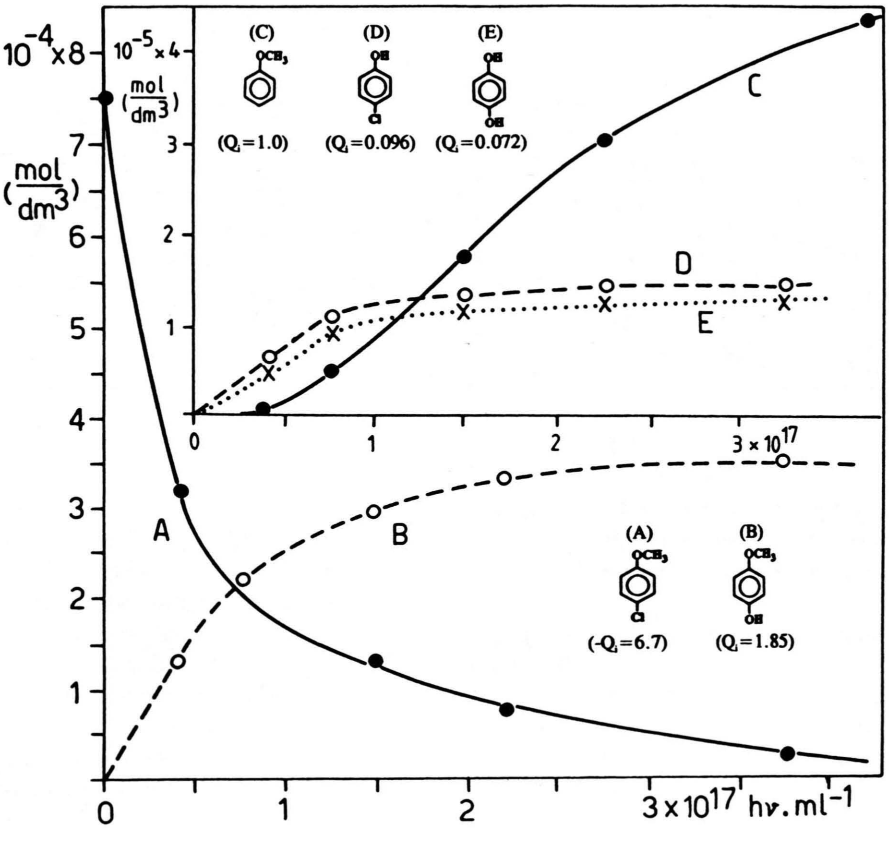


Fig. 5. Photoinduced decomposition of 7.5×10^{-4} mol dm^{-3} 4ClA (A) and formation of 4-methoxyphenol (B), anisole (C), 4-chlorophenol (D), and hydroquinone (E) as a function of absorbed uv-light ($\lambda = 253.7$ nm) at pH 7 in the presence of 2.8×10^{-2} mol dm^{-3} N_2O.

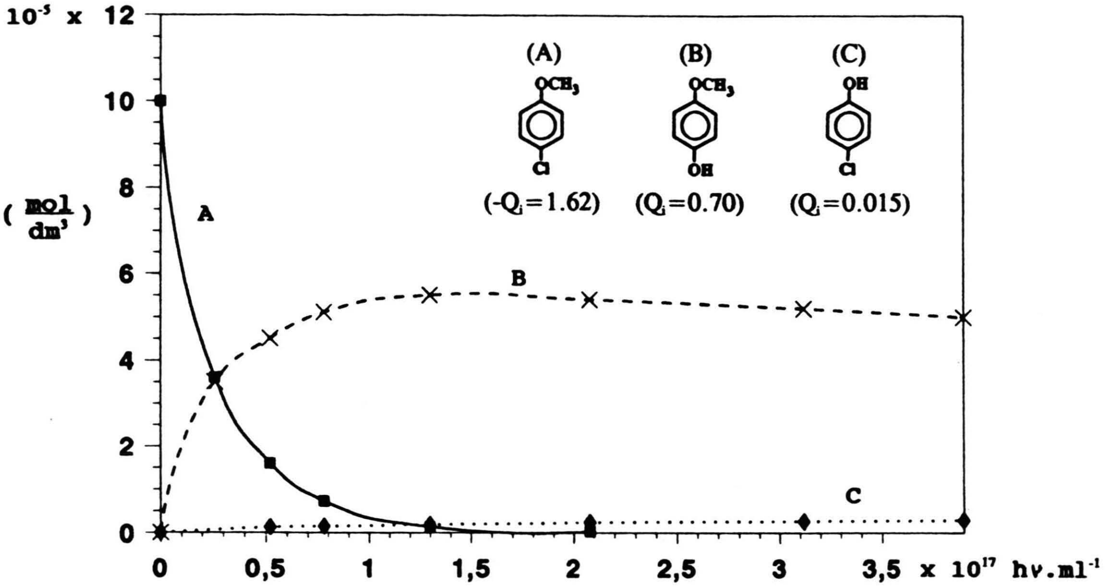
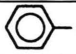


Fig. 6. Photoinduced decomposition of 1.0×10^{-4} mol dm^{-3} 4ClA (A) and formation of 4-methoxyphenol (B), and 4-chlorophenol (C) as a function of absorbed uv-light ($\lambda = 228.8$ nm) in airfree solution at pH 7.

Table 1. Final products obtained by photoinduced decomposition of 4ClA in aqueous solutions under different conditions.

4ClA (mol/dm^3)	λ_{exc} (nm)	pH	Gas	Q_i-values of products				
				Cl$^-$	HO  OCH$_3$	 OCH$_3$	HO  Cl	HO  OH
5.0×10^{-4}	253.7	7	Ar	1.3	–	–	–	–
7.5×10^{-4}	253.7	7	Ar	1.3	0.50	0.10	0.02	–
7.5×10^{-4}	253.7	12	Ar	1.2	0.37	0.075	0.01	–
5.0×10^{-4}	253.7	7	N_2O	2.2	–	–	–	–
7.5×10^{-4}	253.7	7	N_2O	2.4	1.86	–	0.10	–
5.0×10^{-4}	253.7	7	O_2	0.9	–	–	–	0.072
7.5×10^{-4}	253.7	7	O_2	1.1	1.64	–	0.09	–
1.0×10^{-4}	228.8	7	Ar	–	0.70	–	0.015	0.072
5.0×10^{-4}	228.8	9	Ar	1.4	–	–	–	–
7.5×10^{-4}	228.8	7	Ar	1.5	0.82	–	0.07	–

airfree solutions all other products were formed with much higher yields than when using uv-light of $\lambda = 253.7$ nm. The change in the substrate concentration did not affect the product distribution essentially.

All analytical data are summarized in Table 1 for a better illustration.

Generally, the formation of dimers originating from the produced radicals (anisole radical, phenoxy radical and chloroanisole radical cation) were expected, however no such products were found in any of the performed experiments.

4. Discussion

4.1. General Considerations

The subsequently presented reaction mechanisms are derived from the analysis of final products observed under given experimental conditions. In airfree solutions all transients resulting from the photolysis of 4ClA, e.g. e^-_{aq}, H, Cl$^\cdot$ and $^\cdot OCH_3$ etc. have the chance to participate in the reaction events. But, in the presence of N_2O, as is well known, the e^-_{aq} are converted into OH radicals:

$$N_2O + H_2O + e^-_{aq} \rightarrow OH + OH^- + N_2 \qquad (1)$$
$$(k = 0.91 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})$$

In the presence of air (0.25×10^{-3} mol dm^{-3} O_2) as well as solutions saturated with pure oxygen (1.25×10^{-3} mol dm^{-3} O_2) both, e^-_{aq} and H atoms are transformed into peroxy-radicals:

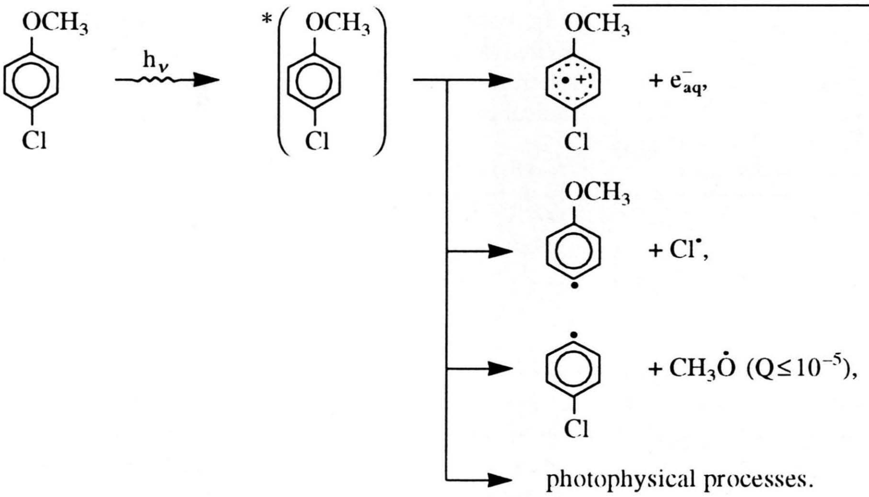
$$O_2 + e^-_{aq} \rightarrow O_2^{\cdot -} \qquad (2)$$
$$(k = 2.1 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})\ [6]$$

$$O_2 + H \rightarrow HO_2^{\cdot} \qquad (3)$$
$$(k_3 = 1.9 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})\ [6]$$

$$HO_2^{\cdot} \rightleftharpoons H^+ + O_2^{\cdot -} \quad (pK = 4.8)\ [7]. \qquad (4)$$

4.2. Airfree 4ClA Solutions

The increasing yield of chloride-ions formed during illumination of airfree 4ClA solutions indicates the extent of decomposition of 4ClA (see e.g. Figure 1). When uv-light of $\lambda = 253.7$ nm is used for irradiation, formation of the S_1-state of 4ClA takes place (Fig. 1, insert I). Consequently, several deactivation pathways can be initiated [8]: formation of radical cations ($4ClA^{\cdot +}$) by electron ejection from substrate, splitting either $Cl^{\cdot}$ or $^{\cdot}OCH_3$, and photophysical processes.



(5a)

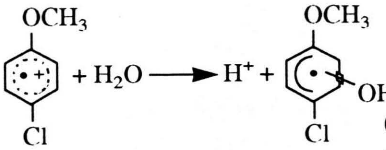
(5b)

(5c)

(5d)

The formation of e^-_{aq} (5a) and of $CH_3O^{\cdot}$ (5c) from anisol has been previously studied [2]. Using $ClCH_2CH_2OH$ as a scavenger for e^-_{aq} and by irradiating the aqueous anisole solutions with uv-light of $\lambda = 253.7$ nm (S_1-state), $Q(Cl^-) = Q(e^-_{aq}) = 0.008$ was found, and when light of $\lambda = 228.8$ nm (S_2-state) was used, $Q(e^-_{aq}) = 0.12$ was observed [2]. However, when N_2O was applied for scavenging e^-_{aq} the following values were found: for S_1-state $Q(e^-_{aq}) = 0.025$ for S_2-state $Q(e^-_{aq}) = 0.120$, respectively [8]. The same e^-_{aq} yields are now assumed for 4ClA.

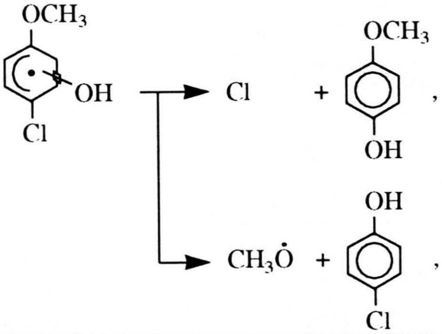
In general it is accepted that radical cations disappear by reaction with water, forming OH-adducts:



(6)

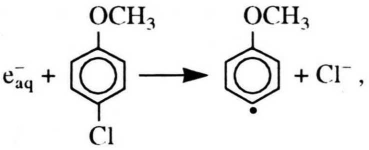
(OH adducts on o-, m-, p- and ipso-positions).

As a consequence of this process a number of consecutive reactions are probable, because they can explain the formation of the measured products (see Table 1):



(7a)

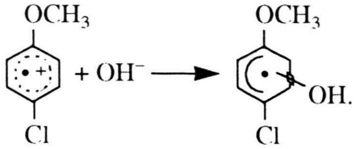
(7b)



(8)

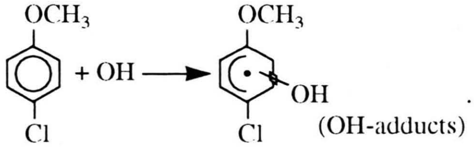
$$Cl^{\cdot} + H_2O \rightarrow H^+ + Cl^- + OH\,. \qquad (9)$$

In alkaline solutions the radical cation reacts with OH^-. For anisole,


(10)

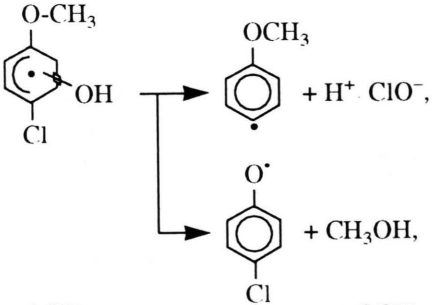
a rate constant $k = 1 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ [9] has been found.

The OH-radicals originating from reactions (5c) and (9) can lead to an additional formation of OH adducts:

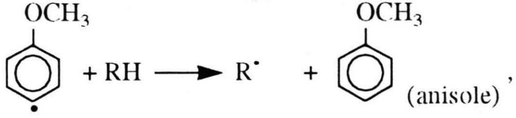


(11)

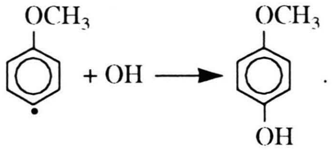
These species can decay according to reaction (7a) and (7b) or following the reactions:


(12a)

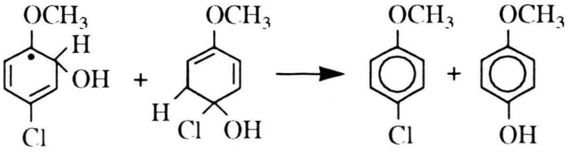
(12b)



(13)


(14)

The phenoxyl radical, $ClC_6H_4O^{\cdot}$, has various resonance structures and its fate was discussed in [10]. The OH-adducts can disappear by disproportionation, e.g. according to

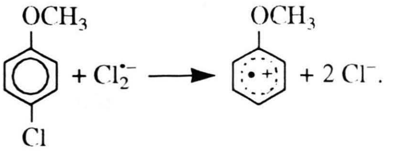


$$+ ClO^- + H^+. \qquad (15)$$

It is also conceivable that a certain fraction of the $Cl^{\cdot}$ atoms reacts with Cl^- ions forming the oxidizing $Cl_2^{\cdot-}$ species:

$$Cl + Cl^- \longrightarrow Cl_2^{\cdot-} \qquad (16)$$

$$k_{16} = 2.1 \times 10^{10} dm^3 mol^{-1} s^{-1},$$

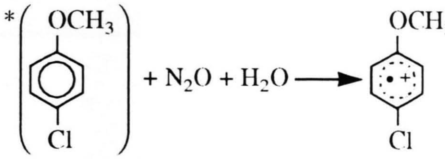

(17)

The so produced $4ClA^{\cdot+}$ can follow reaction (6). Reaction (16) and the resulting consecutive processes may explain the rather high *Q*-yields presented in Table 1. Pulse radiolysis experiments concerning the OH-attack on anisole have been reported in [12].

4.3. 4ClA-Solutions Saturated with N_2O

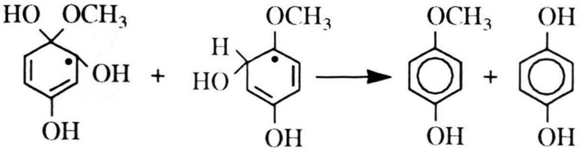
As already mentioned, under these experimental conditions the yield of OH radicals is equal to that of e_{aq}^-, see also reaction (1). Hence, reaction (11), formation of the OH adduct of 4ClA, and all subsequent reactions will play an essential role in the photochemical process of the system under investigation.

It is further very probable that the electronically excited 4ClA-molecules can also react with N_2O by electron transfer, leading to the formation of 4ClA-radical cation and additional OH radicals:



$$+ OH + OH^- + N_2. \qquad (18)$$

Due to this reaction the yields of p-methoxyphenol and p-chlorophenol are increased and also hydroquinone is formed e.g.:

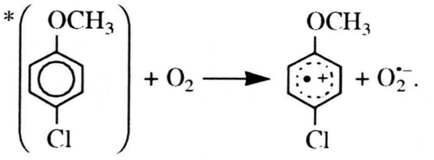


$$+ HCHO + H_2O. \qquad (19)$$

These considerations are in unison with the obtained results (Table 1; also compare curves A and B in Fig. 1, also Fig. 3 with Fig. 5).

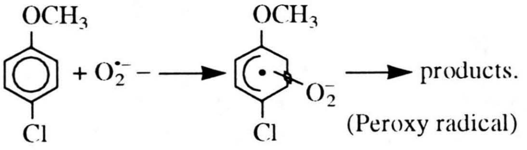
4.4. Oxygenated 4ClA-Solutions

In the presence of oxygen, an adequate process to that expressed by (17) can take place, namely:



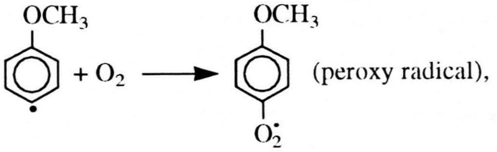
(20)

The radical cation ($4ClA^{\cdot +}$), as shown above, can initiate further reactions. Simultaneously with these processes, e_{aq}^- is reacting with O_2 under formation of $O_2^{\cdot -}$ peroxy-radicals (2). The last ones are able to attack the substrate, forming adducts:

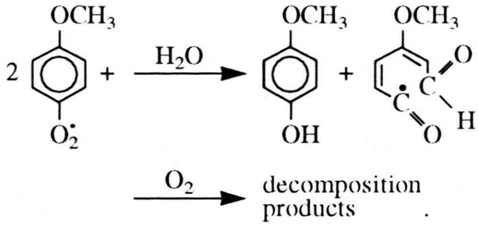


(21)

In addition to this, all radicals present in the solution can be scavenged by O_2 resulting in peroxy radicals, e.g.:



(22)



(23)

Based on these considerations it is obvious that the formation of anisole in the presence of oxygen is not possible (see Table 1).

5. Conclusion

The steady-state photolysis of aqueous 4ClA solutions saturated with Ar, N_2O, air or O_2 was studied in the pH-range from 7 to 12 using uv-light of 253.7 and 228.8 nm.

In airfree solutions anisole, p-chlorophenol and p-methoxyphenol were obtained as products. In solutions saturated with N_2O, air or O_2, no anisole was found, but hydroquinone instead.

The yield of Cl^- ions was considered as an indicator for the photoinduced decomposition process of 4ClA.

With increasing the substrate concentration also the *Q*-values of the products increase.

Rising the pH from 7 to 12 the product yields are decreasing. This can be attributed to the lower activity of $O^{\cdot -}$ species, compared to that of the OH radicals.

The formation of oligomers was also observed, but they were not further investigated.

Acknowledgement

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