Flash Photolysis Studies of 4-Chloroanisole in Aqueous Solution

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Z. Naturforsch. **49a**, 515–521 (1994); received November 15, 1993

The photoinduced formation of transients in aqueous 4-chloroanisole (4ClA), at pH 7 and 9, were studied by conventional flash photolysis. The absorption spectra of various transients in airfree as well as in aqueous solutions saturated with N_2O, air or pure oxygen, are presented and discussed.

Introduction

Photosubstitution of aryl halides has been studied intensively since it was first reported [1], and is still a subject of discussion. Several reaction mechanisms have been proposed [2] to [5]. Steady state studies, for example, suggested that the electron ejection takes place from the lowest triplet state of electronically excited anisole and related aromatic compounds [6]. However, it has been demonstrated that this process occurs from the lowest singlet state in competition with fluorescence [7] to [11] and references therein. The quantum yields (Q) of the photoinduced formation of e_{aq}^- is much higher when the corresponding molecule (e.g. anisole) is excited in its S_2 state [10]. In this case, the photoinduced electron ejection process occurs from each vibration niveau of the S_2 state [11]. Kinetic laser spectroscopic studies in combination with conductivity measurements of 4-chloroanisole (4ClA) and 4-fluoranisole (4FA) in anhydrous and aqueous acetonitrile and t-butanol have also been reported [12]. In t-butanol-water mixtures the formation of e_{aq}^- was also observed.

Very recently, we reported results concerning the steady state photolysis of aqueous 4ClA (pH 7) using monochromatic UV-light of 228 nm and 253.7 nm [13]. The quantum yields of the final products obtained in deoxygenated solutions, as well as solutions saturated with N_2O or oxygen, were determined by HPLC. 4ClA was selected as a representative of halogenated aromatic compounds occuring as pollutants in industrial wastewaters.

The aim of the present study is to improve our understanding of photoinduced formation of transients from 4ClA in aqueous solutions.

Experimental

All solutions were prepared using triply distilled water and p.A. chemicals (Merck or Aldrich). The water was first saturated with the respective gas (high purity argon, N_2O, or O_2) for about 1 hour, then 4ClA was added. The dissolution of the substrate was facilitated by ultrasound. The concentration of the solution was measured spectrophotometrically.

The transient absorption spectra were recorded using a modified conventional flash photolysis computerized equipment (Northern Precision, London) a digital oscilloscope (HP 54600 A), a monochromator Kratos and a PM 3320/40 photomultiplier tube in conjunction with a ESCOM 386 [9, 14]. An air-filled (1 m bar) flash lamp (20 cm) provided light pulses of 5–7 μs duration. In all experiments a discharge voltage of 8 kV was applied.

Results and Discussion

The absorption spectrum of aqueous 1×10^{-4} mol dm^{-3} 4ClA (pH 7) shows maxima at 230, 280 and < 200 nm (Figure 1 B). The transient absorption spectrum resulting from 5×10^{-4} mol dm^{-3} 4ClA in airfree solution at pH 9 is presented in Figure 1 A. It shows several absorption maxima. Based on the fact that 4ClA is excited by the UV-part of the flash light into its S_1 and S_2 states various photophysical and chemical processes can be initiated:

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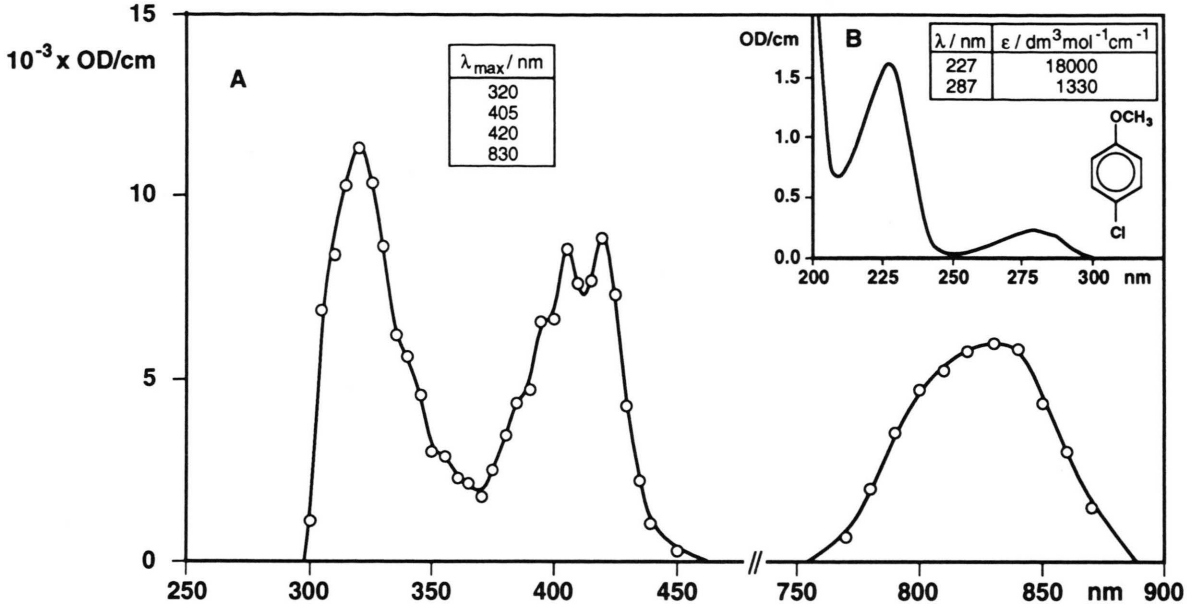
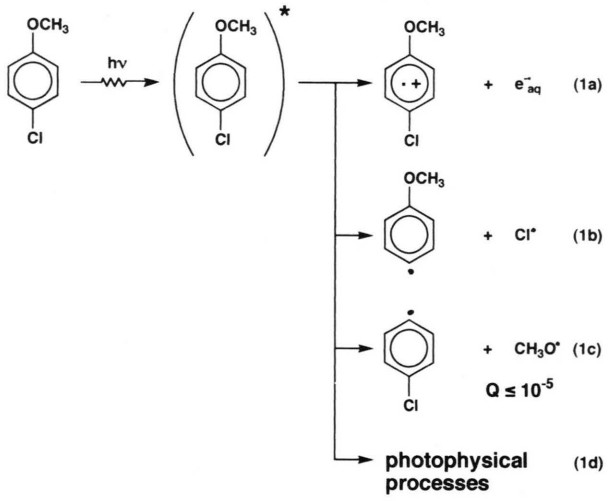


Fig. 1. A) Transient absorption spectrum resulting from 5.0×10^{-4} mol dm^{-3} 4ClA in airfree aqueous solution, pH = 9, 150 μs after flash. B) Absorption spectrum of 1.0×10^{-4} mol dm^{-3} 4ClA in water, pH = 7.



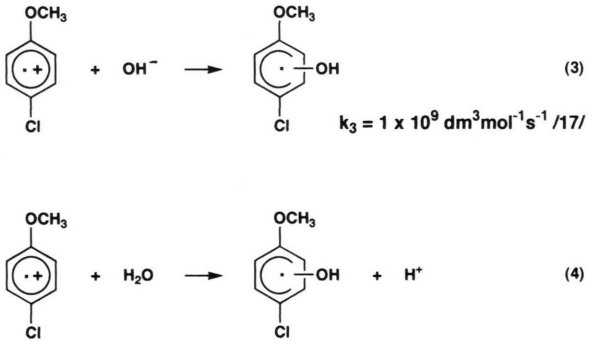
Therefore, the observed transient absorption spectrum in Fig. 1 A is composed of several superimposed, absorption spectra representing various transients (reactions 1a to 1c). The strong absorption of e^-_{aq} at 720 nm ($\varepsilon = 18\,600$ dm^3 mol^{-1} cm^{-1} [15] could not be observed, since the spectrum in Fig. 1 A was measured 150 μs after the light at a time when the reaction [2]

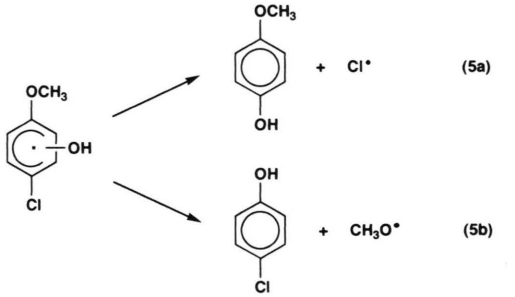
$$ClC_6H_4OCH_3 + e^-_{aq} \rightarrow Cl^- + \dot{C}_6H_4OCH_3 \qquad (2)$$

($k_2 = 9.6 \times 10^9$ dm^3 mol^{-1} s^{-1} [16].

is practically completed.

The radical cation (1 a) can lead to the formation of OH-adduct, (3) and (4), which subsequently can result in 4-methoxyphenol (5 a) or 4-chlorophenol (5 b).





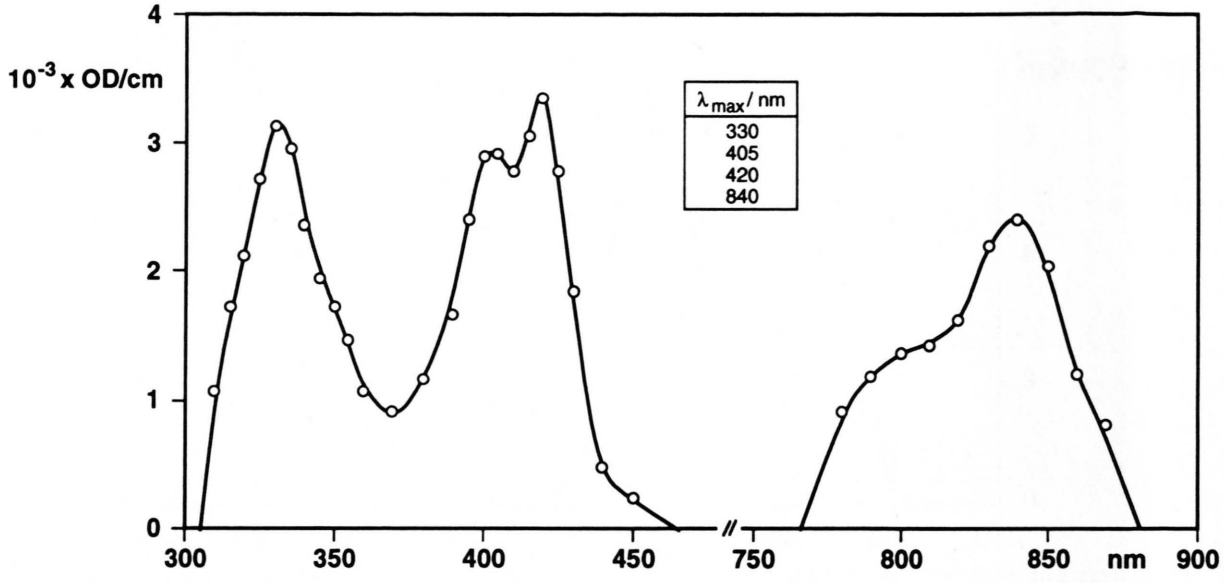
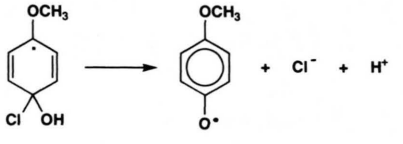


Fig. 2. Transient absorption spectrum recorded by flash photolysis of 5.0×10^{-4} mol dm^{-3} 4ClA in the presence of N_2O (2.8×10^{-2} mol dm^{-3}), pH = 7, 150 µs after flash.

The Cl atom formed by reaction (5a) reacts with water yielding OH radicals:

$$Cl + H_2O \rightarrow OH + H^+ + Cl^- . \qquad (6)$$

It has been found by pulse radiolysis in combination with conductivity measurements that the OH-adduct at the ipso-position to Cl-atom leads to phenoxylradical and Cl^- formation within 10 µs by a first order reaction ([18] and references therein):



(7)

Considering the quantum yields of e_{aq}^- of anisole, $Q = 0.03$ for S_1^- and 0.10 for S_2-state ([11] and references therein) and the subsequent reactions (3), (4), and (6) an essential yield of OH-adducts is expected.

In addition to the above mentioned singlet states also the triplet state of system under investigation might play a role. Therefore, experiments with airfree cyclohexane solution of 4ClA were performed under the same conditions. Based on the lack of any absorption it is concluded that the triplet state of 4ClA is not essentially involved in the reaction mechanisms.

In order to simplify the reaction mechanism by converting e_{aq}^- into OH radical a set of experiments were performed using 4ClA solutions saturated with N_2O. In addition, a part of the electronically excited substrate molecules (4ClA*) could possibly react with N_2O [11, 19].

$$N_2O + e_{aq}^- \rightarrow OH + OH^- + N_2 \qquad (8)$$
$$(k_7 = 0.91 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ [20]}$$

$$(ClC_6H_4OCH_3)^* + N_2O \rightarrow ClC_6H_4OCH_3^{\cdot +} + OH + OH^- + N_2 . \qquad (9)$$

Hence, the transient absorption spectrum presented in Fig. 2 should predominately resemble the 4ClA–OH adducts. At the time of measurement of the spectrum (150 µs after flash) reactions (3) and (4) as well as the reaction

$$ClC_6H_4OCH_3 + OH \rightarrow ClC_6H_4OCH_3{-}OH \qquad (10)$$
(OH-adduct)
$$k = 6.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ [16]}$$

are practically completed. The spectrum presented in Fig. 2 shows several maxima and is similar to that obtained by pulse radiolysis of 4ClA under comparable conditions [16].

In order to favour the formation of the 4ClA-radical cation ($4ClA^{\cdot +}$) an adequate amount of $K_2S_2O_8$ was added as mediator, whereby e_{aq}^- are converted

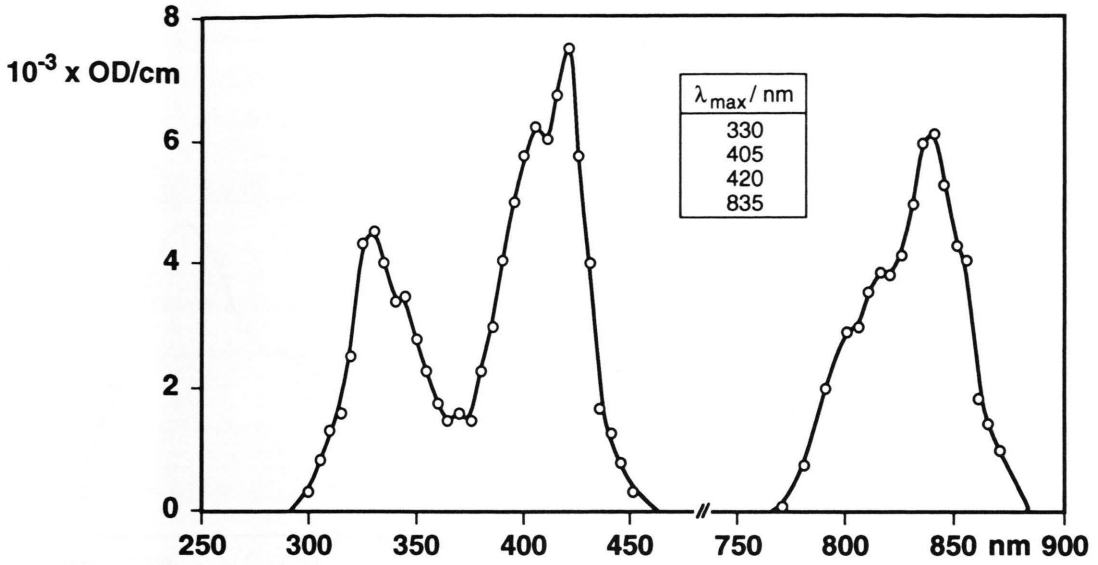


Fig. 3. Transient absorption spectrum resulting from 5.0×10^{-4} mol dm^{-3} 4ClA in the presence of 3.0×10^{-3} mol dm^{-3} $K_2S_2O_8$ in airfree solution, pH = 7, 150 μs after flash.

into the oxidizing $SO_4^{\cdot -}$ species:

$$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^{\cdot -} + SO_4^{2-} \qquad (11)$$
$$k_{11} = 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ [21]}$$

$$4\text{ClA} + SO_4^{\cdot -} \rightarrow 4\text{ClA}^{\cdot +} + SO_4^{2-} . \qquad (12)$$

The $4\text{ClA}^{\cdot +}$ species formed by (1 a) are also included in this case. The transient absorption spectrum obtained in the presence of 5×10^{-4} mol dm^{-3} 4ClA and 3×10^{-3} mol dm^{-3} $K_2S_2O_8$ in airfree solution is presented in Fig. 3. It shows a number of absorption bands between 300 and 880 nm. This spectrum is also obviously superimposed, including the transient $\dot{C}_6H_4OCH_3$ (1 b) and $\dot{C}_6H_4Cl$ (1 c).

It is important to note that the photoinduced formation of the radical cation of anisole in aqueous solution (pH = 1.45) has previously been reported and shows two maxima at 330 and 430 nm [10]. In the present case (pH = 7) the observed absorption bands at 330 nm and 420 nm (Fig. 3) can be attributed to the radical cation, $4\text{ClA}^{\cdot +}$, as a result of reaction (1 a) and (12). The absorption band with a maximum at 835 nm is now observed for the first time.

In order to exclude the action of the OH radicals formed by reaction (6) 1×10^{-2} mol dm^{-3} methanol was added to the solution as a scavenger. Otherwise the same components were present.

$$CH_3OH + OH \rightarrow \dot{C}H_2OH + H_2O \qquad (13)$$
$$k_{13} = 0.95 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ [22]}$$

The resulting transient absorption spectrum is given in Figure 4. It shows practically the same absorption bands as in Figure 3. In the UV-range, however, two new weak peaks (334 and 350 nm) appear. This fact indicates that the contribution of OH-adducts to the spectrum of $4\text{ClA}^{\cdot +}$ species is negligible, but the $\dot{C}H_2OH$ species can react to a small extend [23]. In order to scavenge e_{aq}^- and eventually formed H-atoms as well as other radicals, e.g. C_6H_4Cl, $\dot{C}_6H_4OCH_3$, solutions of 5×10^{-4} mol dm^{-3} 4ClA were saturated with air (0.25×10^{-3} mol dm^{-3} O_2).

$$e_{aq}^- + O_2 \rightarrow O_2^{\cdot -} \qquad (14)$$
$$k_{14} = 1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ [24]},$$

$$H + O_2 \rightarrow HO_2^{\cdot} \qquad (15)$$
$$k_{15} = 2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ [25]},$$

$$HO_2^{\cdot} \rightleftarrows H^+ + O_2^{\cdot -} \qquad (16)$$
$$\text{pK} = 4.8 \text{ [26]},$$

$$\dot{C}_6H_4OCH_3 + O_2 \rightarrow CH_3O\text{-}C_6H_4\text{-}\dot{O}_2 \qquad (17)$$
(peroxy-radical).

The measured transient spectrum under these conditions is presented in Figure 5. It is almost the same as that shown in Figure 1. The intensity of the absorption bands at 320, 405 and 420 nm are practically the same. However, the absorption at 830 nm in Fig. 1 is by a factor of 2 higher than that in Figure 5. In addition, the shapes of the maxima are slightly different.

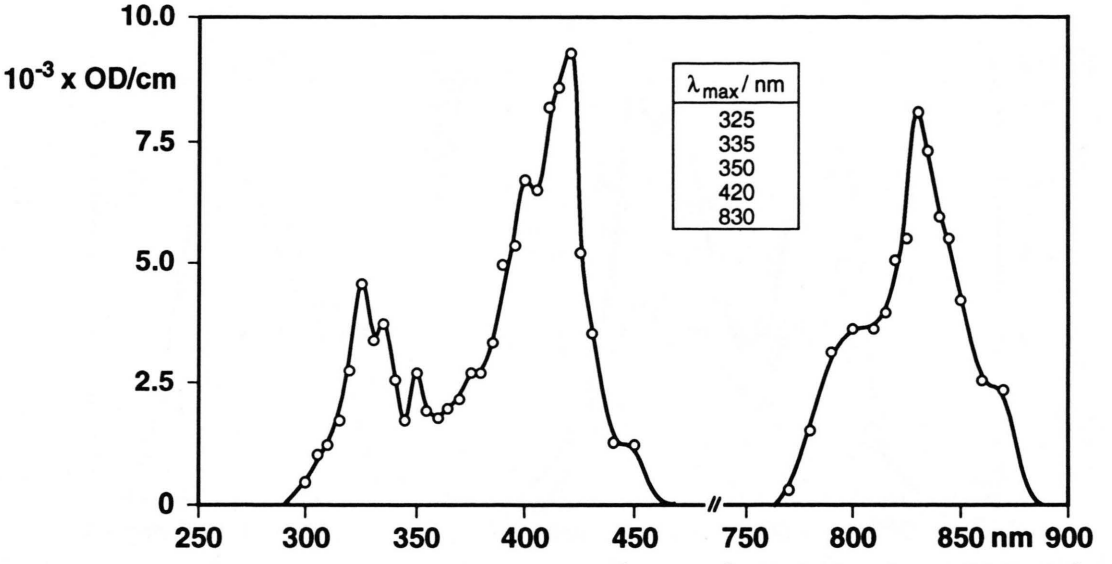


Fig. 4. Transient absorption spectrum resulting from 5.0×10^{-4} mol dm^{-3} 4ClA in the presence of 3.0×10^{-3} mol dm^{-3} $K_2S_2O_8$ and 1.0×10^{-2} mol dm^{-3} CH_3OH in airfree solution, pH = 7, 150 μs after flash.

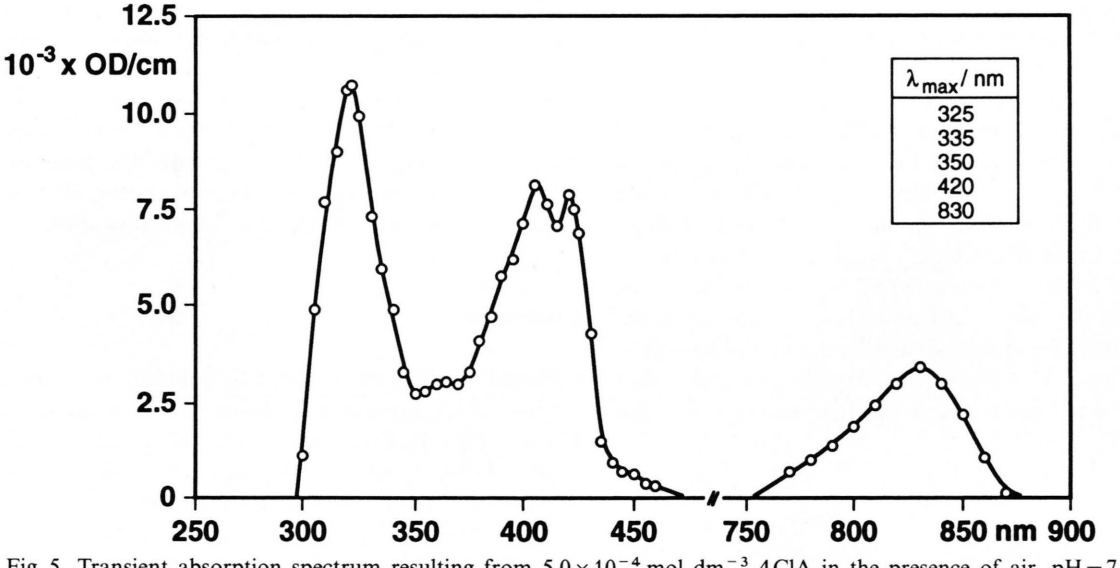


Fig. 5. Transient absorption spectrum resulting from 5.0×10^{-4} mol dm^{-3} 4ClA in the presence of air, pH = 7, 150 μs after flash.

Based on the experimental conditions applied in the case of Figs. 1 and 5, it can be concluded that the spectrum in Fig. 5 mainly consists of the radical cation ($4ClA^{\cdot +}$) and peroxy-radicals formed, e.g., by addition of O_2 to $\dot{C}_6H_4OCH_3$ species (17).

If one assumes that the splitting of the CH_3O-group of 4ClA, see reaction (1c), is as low as in the case of anisole ($Q \sim 10^{-5}$ [1] and references therein then the formation of the $\dot{C}_6H_4Cl$ radical can be ignored. Hence, the $\dot{C}_6H_4OCH_3$ species becomes important. It seems, therefore, very likely that the major absorption of this radical is at 320 nm with somewhat weaker absorptions at 405 and 830 nm (Figure 5). The rest of the absorption spectrum can be attributed to the

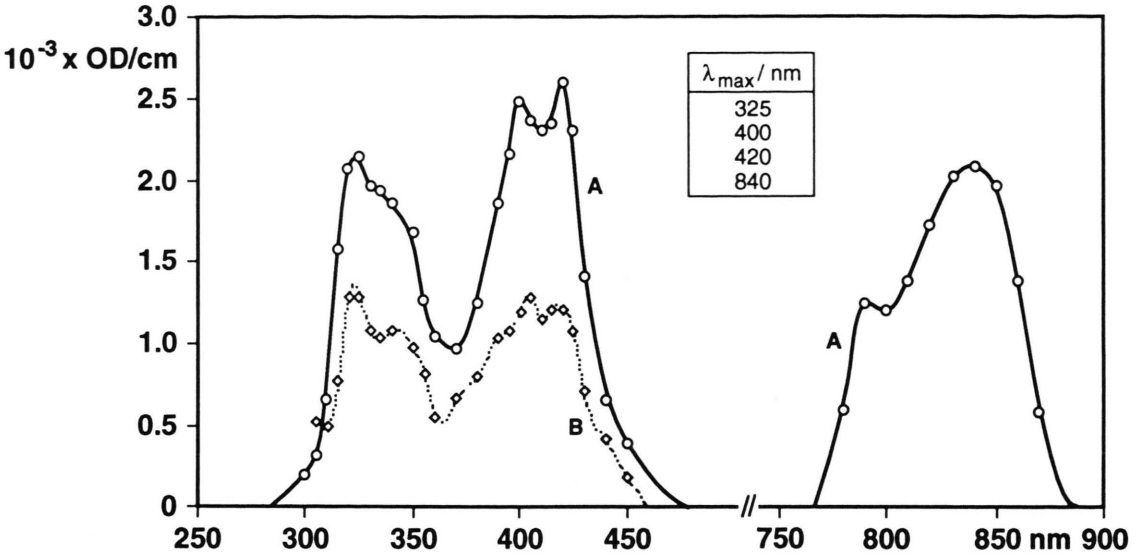


Fig. 6. Transient absorption spectrum resulting from 5.0×10^{-4} mol dm^{-3} 4ClA in the presence of 1.25×10^{-3} mol dm^{-3} O_2, pH = 7, 150 μs (A) and 700 μs (B) after flash.

$4ClA^{\cdot +}$ transients (compare Figs. 1, 3, and 5). This is also in agreement with the previously observed spectrum of $4ClA^{\cdot +}$ in the UV-range [10].

Using 5×10^{-4} mol dm^{-3} 4ClA solutions saturated with pure oxyen (1.25×10^{-3} mol dm^{-3} O_2) an absorption spectrum is obtained (Fig. 6) which is rather similar to that observed in the presence of N_2O (Fig. 2). In the first case e_{aq}^- is converted into OH, see (8), and in the second one $O_2^{\cdot -}$ species are resulting, reaction (16). Both, OH and $O_2^{\cdot -}$ are leading to the formation of cyclohexadienyl type adducts on o-, m-, p- and ipso- positions on the aromatic ring with rather similar absorption characteristics, see reaction (10) and (18):

(18)

In addition to this, $O_2^{\cdot -}$ can be consumed by $4ClA^{\cdot +}$ transient formed by reaction (1a), resulting in the starting compound and O_2 by electron transfer:

$$4ClA^{\cdot +} + O_2^{\cdot -} \rightarrow 4ClA + O_2 . \qquad (19)$$

This back-reaction leads to a strong decrease of the absorption band intensity, as shown in Figure 6. Simultaneously, O_2 is scavenged by radicals present in the bulk of the solution, e.g. by $C_6H_4OCH_3$ (17) leading to the formation of peroxy-radicals. The latter are relatively long-lived species. This is demonstrated by spectrum B of Fig. 6, measured 700 μs after flash.

Conclusion

Based on the results gained by common flash photolysis under various conditions it was possible to obtain the absorption spectra of several transients: $4ClA^{\cdot +}$, 4ClA–OH, $4ClAO_2^{\cdot -}$ mixed with $\dot{O}_2C_6H_4OCH_3$. The findings, as well as the very recently published yields of final products resulting from the 4ClA-photolysis at 228.8 and 253.4 nm [13], contribute to the understanding of the photoinduced degradation of this substrate.

Acknowledgement

Dr. F. S. M. Abd El-Hameed would like to express her thanks to the Austrian Authorities (OAD) for providing a fellowship to work at the University of Vienna, Austria.

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