

Photolysis of 4-chloroanisole in the presence of oxygen Formation of the 4-methoxyphenylperoxyl radical

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Abstract

The photochemistry of 4-chloroanisole was studied in cyclohexane, with and without molecular oxygen. The triplet state is the main transient in argon purged solutions. In air equilibrated conditions the triplet state was not detected and a new broad absorption band was observed above 450 nm. This absorption was assigned to the 4-methoxyphenylperoxyl radical. The formation of phenylperoxyl radicals after direct photolysis of the parent chlorinated compound in the presence of oxygen is reported here for the first time. Anisole is one of the main photoproducts in both conditions. Bicyclohexane was detected only in argon purged conditions while cyclohexyl ether is only formed in the presence of molecular oxygen. The formation of phenylperoxyl radicals after direct photolysis of chloroaromatics can be used to detect the homolytic cleavage of the C–Cl bond.

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1. Introduction

Photochemical transformation is one of the main dissipation processes of pesticides in environmental conditions [1]. Pesticides are an extremely heterogeneous group of chemical compounds and, in many cases, possess two or more functional groups. Given the multiplicity of the chemical structures of pesticides and the complexity of the environmental systems, it is difficult to make predictions, for other pesticides and other situations, from the photochemical results obtained for a specific compound in a specific condition. One approach is to study the photochemistry of a chromophoric chemical group, common to several pesticides, in controlled conditions. The knowledge of the photoproduct distributions and transients of a given chromophore can then be used as a starting point to predict the photodegradation in natural conditions and to assess the photochemical behavior of other pesticides containing the chemical group under study.

The 4-chlorophenoxy group is a chromophore shared by several pesticides. The photodegradation of these compounds in solution and on the solid/gas interface is mainly due or mainly related to this chromophoric system [2–8]. The detailed knowledge of the photochemistry of this group, namely the final photoproducts and radicals formed after irradiation, can be used as a starting point to understand the photochemistry of other 4-chlorophenoxy pesticides. However, even the photochemistry of 4-chloroanisole (4-CA), a good model molecule for the chlorophenoxy chromophore, is still under debate [9–13]. It has been proposed that the main primary photoreaction step of chlorophenoxy compounds in non-polar solvents is the homolytic cleavage of the C–Cl bond. In polar environments both the homolytic and the heterolytic cleavages occur [9–11]. The formation of the 4-CA radical cation was also proposed in acetonitrile [12]. However, very few transient absorption studies of 4-CA have been published [12,13]. Even in cyclohexane, where it is well accepted that the homolytic cleavage is the main reaction pathway, no transient absorption study was performed.

In this work, the photochemistry of 4-CA in cyclohexane was studied using laser flash photolysis and chromatography techniques. The main degradation products and transients were identified and a reaction scheme is proposed.

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2. Experimental

2.1. Materials

4-CA, anisole, 4-methoxyphenol (Aldrich); cyclohexane (Merck Uvasol), methanol and acetonitrile (Merck Lichrosolv) were used without further treatment. Water was deionized and distilled.

2.2. Methods

2.2.1. Laser flash photolysis system

Laser flash photolysis experiments were carried out with the system described in reference [14] in the transmission mode. The transient absorption data are reported as ΔOD .

2.2.2. Irradiation and product analysis

Photolysis studies were conducted in a system previously used to study 4-chlorophenol and pesticides [2–5]. The irradiation at 254 nm was obtained using a 16 W low-pressure mercury lamp (Applied Photophysics) without filters and without refrigeration.

The analyses were performed by GC–MS using a Hewlett Packard 5890 Series II gas chromatograph with a 5971 series mass selective detector (E.I. 70 eV). A CP-WAX 58CB capillary column with 25 m length, 0.25 mm i.d. and 0.25 μm film thickness (Chrompack) and a DB-35MS capillary column with 30 m length, 0.25 mm i.d. and 0.25 μm film thickness (J&W Scientific) were used. The initial temperature, 50 $^{\circ}\text{C}$, was maintained during 5 min and then a rate of 5 $^{\circ}\text{C}/\text{min}$ was used up to a final temperature of 250 $^{\circ}\text{C}$. Analyses of the main photoproducts were conducted at conversions lower than 5% and studies of control samples kept in the dark during irradiation were also performed.

3. Results and discussion

3.1. Transient absorption

The transient absorption of 4-CA in cyclohexane was first studied in argon purged conditions. At pulse end the spectrum shows a strong absorption band centred at 335 nm (results not shown). This band was already reported [12] and was assigned to the triplet–triplet absorption. Fig. 1 presents the spectra obtained 1 μs after the laser pulse, in oxygen saturated and argon purged conditions. The comparison of the two spectra at 335 nm shows a residual absorption due to the 4-CA triplet state in argon purged conditions. As observed in perfluorohexane [12], the lifetime of the 4-CA triplet state in cyclohexane is shorter than 1 μs .

Fig. 1 also shows that the spectrum obtained in oxygen saturated conditions has a small absorption band centred at 550 nm. This absorption was unexpected. In fact, in previous transient absorption studies of 4-CA, no absorption was detected above 500 nm [12,13]. The longer transient absorption band observed in these studies was detected between 420 and 500 nm and was assigned to the 4-CA radical cation and to a triplet state transient complex [12].

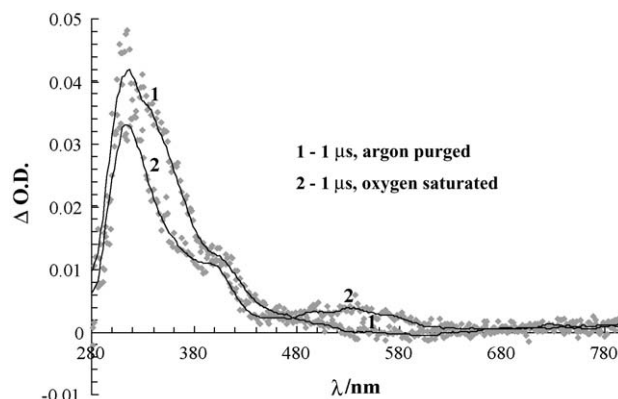


Fig. 1. Time resolved absorption spectra of 4-CA, in argon purged and in oxygen saturated cyclohexane solutions, obtained 1 μs after the laser pulse (266 nm; ~ 30 mJ/pulse; OD ~ 2).

Pulse radiolysis studies of substituted phenyl peroxy radicals showed that the 4-methoxyphenylperoxy radical has a broad absorption in the visible region of the spectrum [15,16]. This radical was produced by reductive debromination of 4-bromoanisole, followed by rapid reaction of the formed phenyl radical with oxygen. Since spectrum 2 of Fig. 1 was obtained in oxygen saturated conditions, the band at 550 nm can be due to the 4-methoxyphenylperoxy radical.

In the conditions studied this radical can be formed after homolytic cleavage of the C–Cl bond, followed by reaction of the methoxyphenyl radical with molecular oxygen. In order to verify this hypothesis we have also studied the transient absorption of 4-CA at pulse end, in air equilibrated and oxygen saturated conditions.

The long wavelength absorption band detected 1 μs after the laser pulse is more intense at pulse end and increases with the oxygen concentration (see Fig. 2). These results confirm the formation of the 4-methoxyphenylperoxy radical. The direct formation of this radical is, as far as we know, reported here for the first time. The absorption band detected is blue shifted in comparison to that obtained in aqueous solution by pulse radiolysis, which showed a maximum near 600 nm [15,16]. However, these radicals are very sensitive to the polarity of the environ-

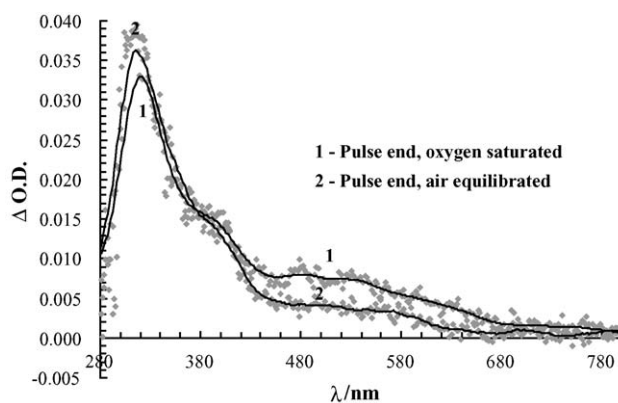


Fig. 2. Time resolved absorption spectra of 4-CA, in oxygen saturated and in air equilibrated cyclohexane solutions, obtained at pulse end (266 nm; ~ 30 mJ/pulse; OD ~ 2).

ment. Blue shifts of about 30 nm have been observed when going from water to methanol [16]. The blue shift observed in cyclohexane is in agreement with this behavior.

The spectra obtained in cyclohexane also show an absorption band with a maximum near 310 nm. The same spectral distribution was obtained for solutions with OD between 0.2 and 2.0. This result indicates that the absorption cannot be due to excimers nor to transients resulting from bimolecular reactions of 4-CA. Since the results were obtained in the presence of oxygen (no triplet is present), this absorption can be due to the methoxyphenyl radical. The absorption of some substituted phenyl radicals is similar in spectral location to that of the parent compounds [17]. The absorption of these radicals is, however, more intense, and shows a small shift to the red [17], which allows for their detection above 300 nm. The decrease in absorption below 300 nm reflects the depletion of 4-CA.

3.2. Photodegradation products

The identification of the main photodegradation products was first performed in the absence of molecular oxygen. Fig. 3a presents the photoproduct distribution obtained in these conditions. The main photoproducts were anisole and bicyclohexane. The identification of the former product was based on the analysis of an authentic sample while the structure assignment of the latter was based on its mass spectrum. The library search (HP nbs54k.l) for the mass spectrum obtained for this product gave a match higher than 90% for the proposed structure.

Anisole has already been reported as a major degradation product of 4-CA in hydrogen donor solvents [9–11]. Bicyclohexane was also detected after the photodegradation of chlorobenzene in cyclohexane [18] and can be accounted for by reactions of the cyclohexyl radical formed after hydrogen abstraction. The photoproduct distribution was also studied in oxygen saturated conditions. The results (see Fig. 3b) strongly differ from those obtained with the argon purged samples. Anisole was also observed in these conditions but bicyclohexane was only detected in trace amounts. Two new products with $m/z = 182$ and 100 are formed in these conditions. The first was assigned to cyclohexyl ether based on its mass spectrum and on a comparison with the database spectra (match higher than 90%), while the latter shows a molecular formula with composition $C_6H_{12}O$. The presence of oxygen in the new products confirms that other reaction pathways are available in air equilibrated and oxygen saturated conditions.

The absence of dimerization products of 4-CA is in agreement with the transient absorption results, which showed a similar spectral distribution for solutions with OD between 0.2 and 2.0.

3.3. Main photodegradation pathways

Previous photochemistry studies of 4-CA in solution [9–11] indicated that the homolytic cleavage of the C–Cl bond is the main reaction pathway in aliphatic solvents. While the radical cation is easily detected by flash photolysis, it absorbs appreciably in the visible region [12], phenyl radicals are expected to show weak absorbance above 300 nm [17]. Aryl cations are

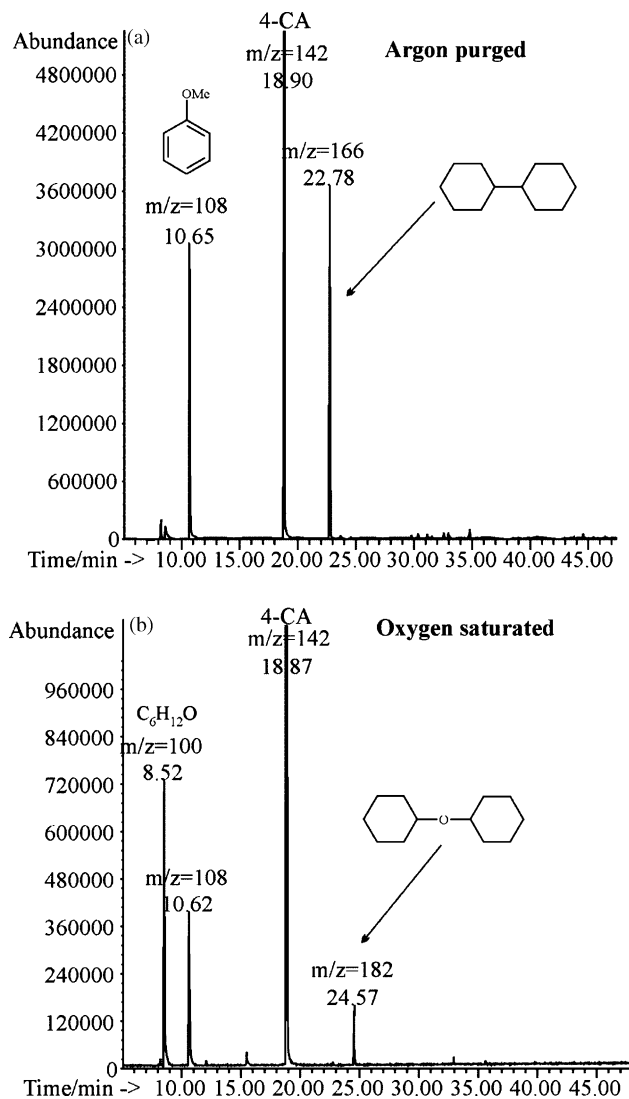


Fig. 3. GC–MS chromatograms of irradiated solutions (254 nm) of 4-CA in cyclohexane: (a) in argon purged conditions; (b) in oxygen saturated conditions.

very reactive species and are also very difficult to detect [19]. Therefore, in situations where the phenyl radical is formed in the presence of molecular oxygen, the homolytic cleavage can be detected by flash photolysis since the correspondent peroxy radicals are quickly formed and these transients absorb in the visible region of the spectrum. Moreover, since the phenyl cation does not interact with molecular oxygen [19] the formation of the peroxy radical can be used to detect the homolytic fission in situations where both kinds of cleavages are expected.

The formation of the methoxyphenylperoxy radical (see Fig. 4) indicates that the homolytic cleavage of the C–Cl bond is the major photodegradation pathway in cyclohexane. Due to the presence of oxygen, the rate constant for the homolytic cleavage should be at least of the same order of that of oxygen diffusion, in order to take place before quenching. This result suggests that the reaction should mainly proceed from the singlet state. In fact, the triplet state was not detected by flash photolysis in these conditions. The triplet state homolysis of Ar–Cl bonds can occur but only when the chloro compound has a triplet energy

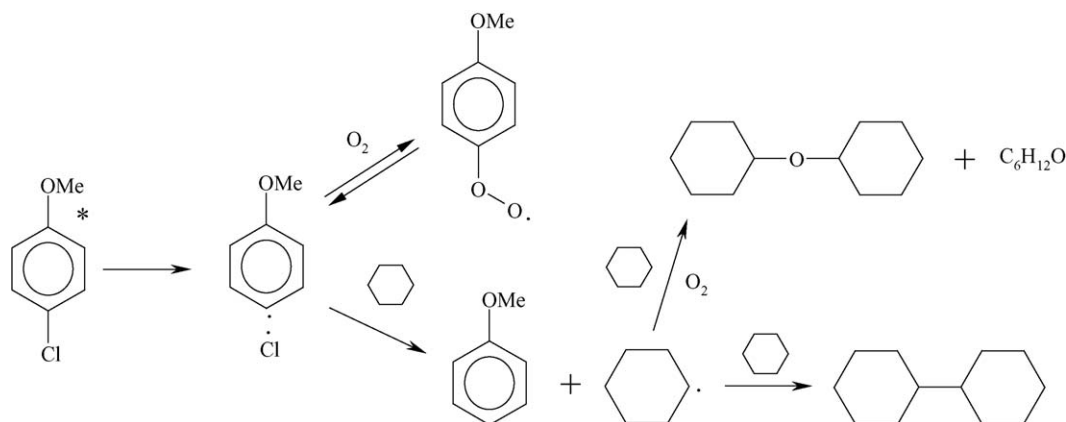


Fig. 4. Main photodegradation pathways of 4-CA in cyclohexane.

close to the necessary bond-dissociation energy [20]. The singlet state energy of 4-CA is 406 kJ mol^{-1} [21] while the triplet energy is 327 kJ mol^{-1} [22]. Considering the value of 398 kJ mol^{-1} for the C–Cl bond-dissociation energy (chlorobenzene [23]), only the singlet state of 4-CA is able to undergo homolytic cleavage.

Hydrogen abstraction from the solvent by the methoxyphenyl radical leads to anisole. However, among the main photodegradation products, this is the only containing the aromatic ring. This result indicates that the peroxy radical is not directly involved in the formation of final photoproducts. Many arylperoxy radicals only decay by second order reaction with other peroxy radicals, leading to an unstable tetroxide which then eliminates O_2 and forms two identical phenoxy radicals [15,16]. These phenoxy radicals would lead to 4-methoxyphenol in hydrogen donor solvents. This compound was not detected in the conditions studied. Therefore, after homolytic cleavage, only the methoxyphenyl radical leads to net reaction. The peroxy radical should establish an equilibrium with the phenyl radical where only the latter reacts (see Fig. 4). This is in agreement with the presence of an isobestic point in Fig. 2.

The cyclohexyl radical can also react with molecular oxygen (see Fig. 4). The absence of bicyclohexane and the corresponding formation of bicyclohexyl ether in oxygen saturated conditions indicates that the differences in the photoproduct distributions are mainly due to the reaction of the cyclohexyl radical with molecular oxygen.

The degradation of 4-CA in air equilibrated conditions suggests that chlorophenoxyl pesticides can undergo photodechlorination in environmental conditions, even in the presence of molecular oxygen.

4. Conclusions

The photochemistry of 4-chloroanisole in cyclohexane is strongly dependent of the presence of oxygen. The triplet state is the main transient in argon purged solutions. In air equilibrated conditions, a new broad absorption, due to the 4-methoxyphenylperoxy radical, was detected. Anisole is one of the main photoproducts in both conditions. Bicyclohexane was detected only in argon purged conditions. Photoproducts containing oxygen were detected only in the presence of molecular

oxygen. The differences in the photoproduct distribution are mainly due to reaction of the cyclohexyl radical with molecular oxygen. The formation of phenylperoxy radicals after direct photolysis of chloroaromatics can be used to detect the homolytic cleavage of the C–Cl bond.

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