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Phototransformation of carbaryl in aqueous solution Laser-flash photolysis and steady-state studies

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Abstract

Aqueous carbaryl is shown to be photolysed with a low quantum yield ($(2.1\pm0.2)\times10^{-3}$ in air-saturated medium) into 1,2-naphthoquinone, 1,4-naphthoquinone, 2-hydroxy-1,4-naphthoquinone and 7-hydroxy-1,4-naphthoquinone. In acetonitrile and methanol, carbaryl is mostly photoconverted into 1-naphthol. This behaviour contrasts with those of carbamates and aryl esters that generally undergo efficient photo-Fries rearrangement. Several transient species were detected by laser-flash photolysis in water: the triplet–triplet (T–T) absorption ($\lambda_{max} = 410$ nm, $k_d = 3.5\times10^5$ s^{-1}), the solvated electrons ($\phi = 0.022\pm0.002$), the naphthoxyl radicals and a long-lived unassigned species. The mechanism of phototransformation is discussed.

Keywords: Carbamate; Photoionisation; T–T absorption; Naphthoxyl radicals; Naphthoquinones; Hydroxynaphthoquinones

1. Introduction

Carbamates constitute an important class of insecticides that are widely used against pest because of their rapid action and moderate persistent in the environment. Their toxicity is due to the carbamylation of acetyl cholinesterase enzyme at nerve endings [1,2]. One of the most popular carbamate insecticides is carbaryl (1-naphthyl-*N*-methyl carbamate) broadly used against harmful insect species on more than 120 differents crops with contact [3]. This compound has a DT_{50} comprise between 7 and 28 days in soil [4] and its biological lifetime in fish is around 6 months [5]. It exhibits a moderate mammalian toxicity; the acute oral LD_{50} for rats is 850 mg kg^{-1} [3], but it is known for its toxicity to honeybees.

Carbaryl absorbs solar radiations and can therefore undergo photodissociation in the environment. Hydrolysis was shown to occur in a moderatly basic medium [6]. According to the literature, photolysis in distilled, pond, natural or artificial sea water under solar and UV radiations ($\lambda > 290$ nm) yields 1-naphthol [6,7] and the quantum yield of photolysis in pure water is low (0.006 at 313 nm) [8]. This behaviour contrasts with those of carbamates and aryl esters that are often reported to undergo efficient photo-Fries rearrangement [9–12,14]. For example, the quantum yield of phototransformation of 1-naphthyl acetate into 2-acetyl-1-naphthol and 4-acetyl-1-naphthol was found to be very high in acetonitrile (0.17) [13]. To better understand the photochemical behaviour of carbaryl in water, we investigated its photolysis by means of steady-state irradiations and laser-flash photolysis.

2. Experimental section

2.1. Chemicals

Carbaryl was purchased from Riedel de Haen (purity 99.7%). 1,4-Naphthoquinone, 1,2-naphthoquinone and 2-hydroxy-1,4-naphthoquinone were purchased from Aldrich. Water was purified using a Milli-Q (Millipore) device. Methanol and acetonitrile were of the highest grade available.

2.2. Steady-state irradiations

In order to minimise hydrolysis, carbaryl was dissolved in water buffered at pH 6.5 using phosphate buffers. For analytical studies, irradiations were performed using a device consisting of six fluorescent tubes (Duke sun lamp) emitting between 280 and 350 nm with a maximum emission located at 310 nm and surrounded by a cylindrical mirror. A cylindrical Pyrex-reactor was placed along the axis of the device. For the quantum yield evaluations, solutions were irradiated in a monochromatic parallel beam using a xenon

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lamp equipped with a Schoeffel monochromator. The cell pathlength was 1 cm. The photon rate fluence was measured using potassium ferrioxalate as a chemical actinometer.

2.3. Laser-flash photolysis

Transient absorption experiments were carried out using a frequency-quadrupled Nd:YAG laser (Quanta-Ray GCR-130, 266 nm). Experimental procedures have been previously described [14].

2.4. Analyses

Irradiated samples were analysed using a Waters chromatograph equipped with a 996-photodiode array detector and a conventional C_{18} reverse-phase (4.6 mm × 250 mm) column. The eluent was methanol–water (0.1% H_3PO_4) mixtures (60:40 v/v). Preparative HPLC was performed on a Gilson apparatus equipped with an UV detector using a semi-preparative microsorb 3 μm column and methanol–water mixtures (60:40 v/v) as mobile phase. UV-Visible spectra were recorded on a Cary 113 spectrophotometer (Varian). ^{1}H NMR spectra were recorded on a Brucker AC400 spectrometer. Fluorescence measurements were performed on a Perkin-Elmer MPF-3L spectrofluorimeter equipped with an IP28 photomultiplier. Chemical ionisation mass spectrometry was conducted on a HP 5989 B mass spectrometer, methane being used as reagent gas.

3. Results

3.1. Fluorescence

The absorption and emission spectra of carbaryl in water are given in Fig. 1. The absorption band exhibits a maximum at 280 nm and extends up to 320 nm. The fluorescence emission band is broad, extending from 310 to 390 nm with a maximum at 330 nm. The emission decay was monitored at 380 nm by laser-flash photolysis. As seen in Fig. 2, the emission was observed within the first 200 ns following the pulse end in deoxygenated medium. The decay followed a first-order kinetics with $k = (3.0 \pm 0.3) \times 10^7\ \mathrm{s}^{-1}$. It can be deduced that the lifetime of singlet excited state is equal to 33 ± 3 ns. In oxygen-saturated medium, the decay was slightly accelerated and the lifetime was equal to 26 ± 2 ns.

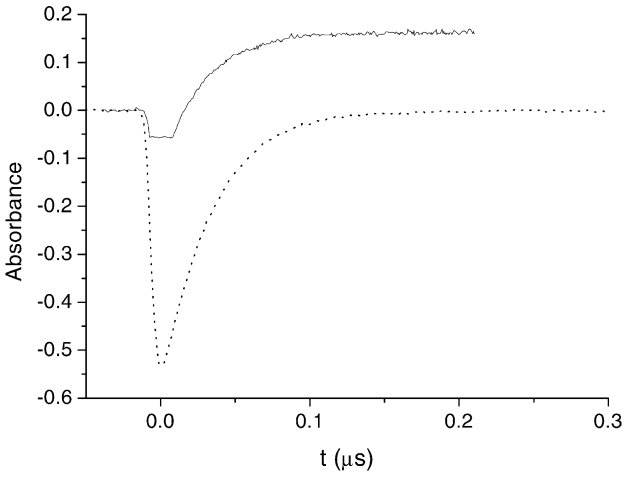


Fig. 2. Time course emission at 380 nm (· · ·) and time course absorbance at 410 nm (—) from deoxygenated aqueous carbaryl (10^{-4} M).

3.2. Transients species

The laser-flash photolysis of deoxygenated aqueous carbaryl (10^{-4} M) yielded several transient species as shown in Fig. 3. The characteristic absorption of solvated electrons ($\lambda_{max} = 725$ nm) was detected during the three 3 μs follow-

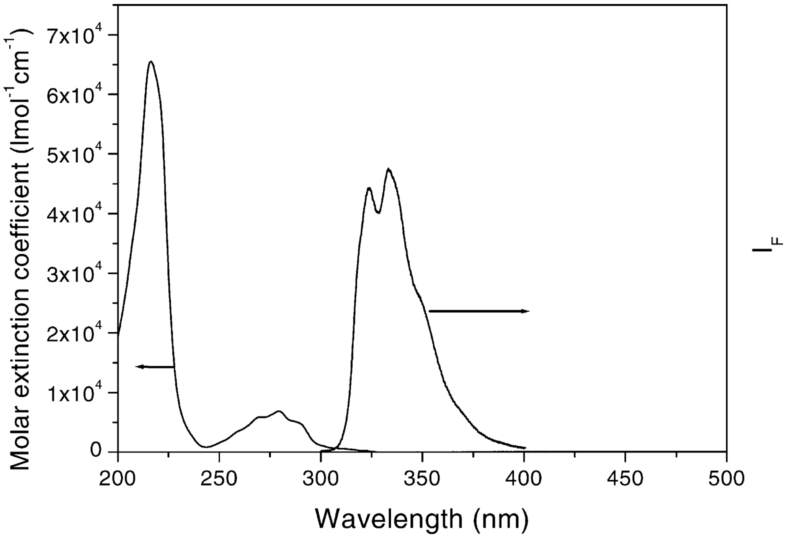


Fig. 1. Absorption and emission spectra of carbaryl (10^{-4} M) in water.

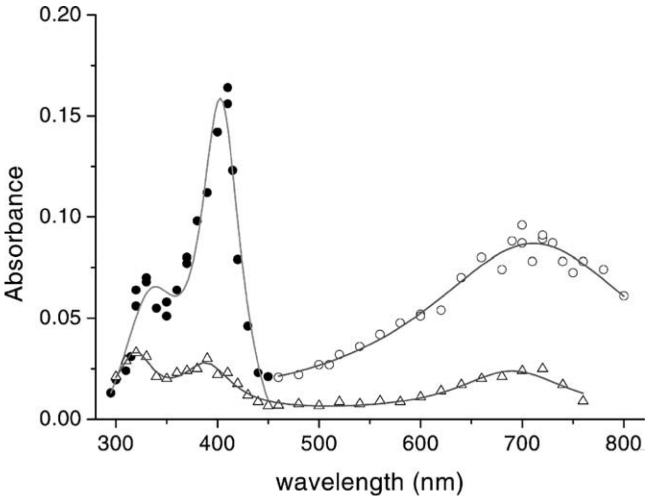


Fig. 3. Transient absorption spectra from deoxygenated aqueous carbaryl (10^{-4} M). (○) Difference between absorbances measured at pulse end and 3 µs after; (●) difference between absorbances measured 0.2 and 9 µs after the pulse end; (△) absorbance measured 9 µs after the pulse end.

ing the pulse end. Another transient absorption band could be observed at shorter wavelength during the first 9 µs following the pulse. It showed a maximum at 410 nm and a shoulder around 340 nm. The rate of formation at 410 nm was close to the rate of the singlet decay (see Fig. 2). A third transient absorption could be detected by monitoring the absorbance 9 µs after the pulse end, i. e. after the complete disappearance of the two short-life species. It showed maxima at 320, 390 and 690 nm. This species showed a lifetime of about 20 µs.

Carbaryl (10^{-4} M) was also photolysed in oxygen-saturated medium. The decay rate of the third species was not affected by the presence of oxygen. In contrast, the decay rates of the solvated electrons and of the 410-nm transient were significantly enhanced. The latter decayed by a first-order kinetics with a rate constant equals to $(2.6 \pm 0.3) \times 10^6\,\mathrm{s}^{-1}$ against $(3.5 \pm 0.3) \times 10^5\,\mathrm{s}^{-1}$ in deoxygenated medium. We noticed that the absorbance decreased much less rapidly at 335 nm than at 410 nm (Fig. 4), and the decay at 335 nm was better fitted by a second-order kinetics ($2k/\varepsilon = (2.5 \pm 0.7) \times 10^7\,\mathrm{cm\,s}^{-1}$) than by a first-order kinetics (inset of Fig. 4). It suggests the existence of a fourth transient species. Its transient absorption spectrum was obtained by substracting absorbancies measured at 2 and 9 µs after the pulse end ($A^{2\,\mu\mathrm{s}} - A^{9\,\mu\mathrm{s}}$) in oxygen-saturated medium, i.e. after the complete disappearance of the 410-nm transient (Fig. 5). The maximum of absorption of this fourth transient was located at 335 nm, the shoulder observed around 340 nm in the absence of oxygen may correspond to it. Unfortunately, this hypothesis could not be firmly proved because in the absence of oxygen the decay rates at 410 and 335 nm were very close and the 335-nm transient cannot be observed alone.

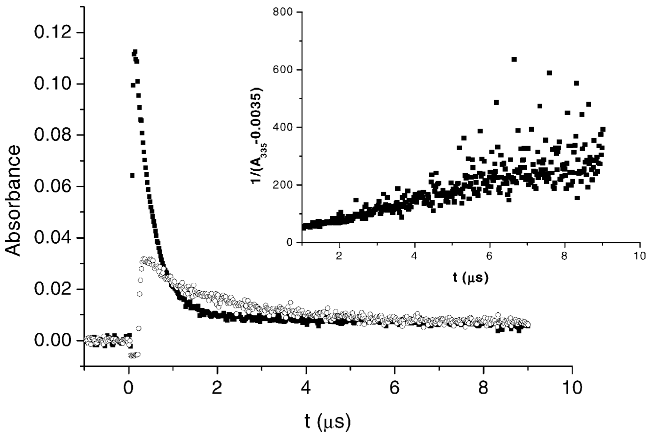


Fig. 4. Time course absorbances from oxygen-saturated solution of carbaryl (10^{-4} M) at 410 nm (■) and 335 nm (○). Inset: linearisation of the decay at 335 nm assuming a second-order kinetics.

The difference $A^0 - A^{3\,\mu\mathrm{s}}$ at 700 nm that corresponds to the absorption of solvated electrons increased in a quadratic way with the energy pulse, P (Fig. 6). Plot of $(A^0 - A^{3\,\mu\mathrm{s}})/P$ versus P gave a linear regression showing that electrons arose from both mono- and biphotonic processes. From the intercept that is related to the monophotonic process and using chemical actinometry, we got $(\varepsilon \times \phi)_{700} = 400 \pm 50\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$. Based on $\varepsilon = 18300\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, we compute $\phi = 0.022 \times 0.002$. In contrast, the difference $A^{0.2\,\mu\mathrm{s}} - A^{9\,\mu\mathrm{s}}$ at 410 nm increased linearly with P as expected for a monophotonic formation. From the slope value, we deduced $(\varepsilon \times \phi)_{410} = 3700 \pm 300\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$.

The 410-nm absorption can be assigned to the triple–triplet (T–T) absorption. This assignment is supported by the scavenging effect of oxygen and by the fact that the formation rate of the 410-nm absorption is equal to the decay rate of the excited singlet. Moreover triplet excited states of naphthalene and hydroxy or methyl derivatives also show

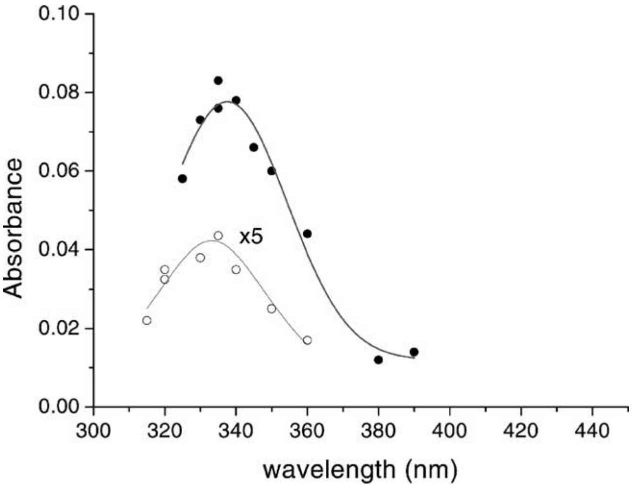


Fig. 5. Transient spectrum measured oxygenated solution of carbaryl, difference between absorbances measured 2 and 9 µs after the pulse end (○). Transient spectrum of naphthoxyl radical measured from an oxygen-saturated aqueous solution of naphthol, absorbance measured at pulse end (●).

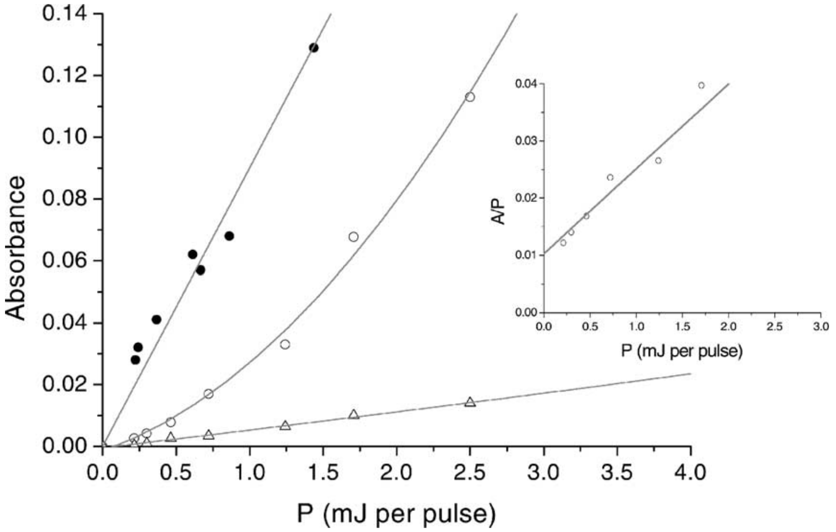


Fig. 6. Dependence of absorbances on P: (○) $A^0 - A^{3\,\mu s}$ at 700 nm; (△) $A^{3\,\mu s}$ at 700 nm; (●) $A^{0.2\,\mu s} - A^{9\,\mu s}$ at 410 nm. Inset: plot of A/P vs. P.

maximum between 415 and 435 nm in polar solvent. The high $\varepsilon \times \phi$ value indicates that the triplet excited state is efficiently populated as generally observed for naphthalene and derivatives [15].

The 335-nm transient that decayed by a second-order kinetics is likely to be the naphthoxyl radical. To confirm this assignment, we produced the naphthoxyl radical by photolysing naphthol in water. As expected the transient absorption observed along with solvated electrons exhibited a maximum at 335 nm (Fig. 6) and decayed by a second-order kinetics with $2k/\varepsilon = (1.3 \pm 0.1) \times 10^7\,\mathrm{cm\,s^{-1}}$. The ratio of the end pulse absorbances at 700 and 335 nm was found to be equal to 2.0 ± 0.1. Using this value and the molar absorption coefficient of solvated electrons at 700 nm, we computed $\varepsilon_{335} = 9000 \pm 500\,\mathrm{M^{-1}\,cm^{-1}}$ for the naphthoxyl radical and we could estimate the yield of formation of naphthoxyl radical from carbaryl as being between 0.01 and 0.02.

At last, the transient showing absorption maxima at 320, 390 and 690 nm and no reactivity toward oxygen might be the radical cation produced after electron ejection.

3.3. Steady-state irradiation

The quantum yield of photolysis at 280 nm was found to be equal to $(2.1 \pm 0.2) \times 10^{-3}$ in air-saturated medium. As shown on Fig. 7, we mainly observed the formation of oxidation photoproducts. 1,2-Naphthoquinone, 2-hydroxy-1,4-naphthoquinone and 1,4-naphthoquinone

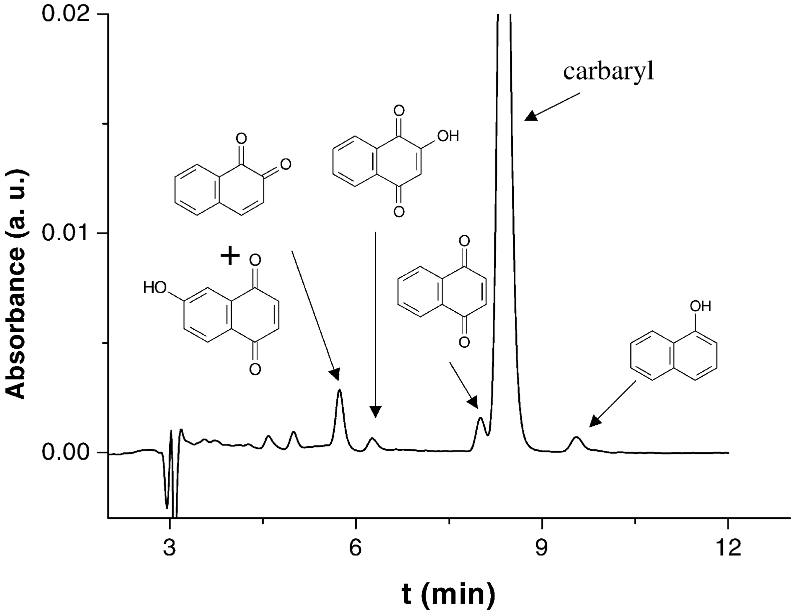


Fig. 7. HPLC chromatogram of an air-saturated solution of carbaryl (10^{-4} M) irradiated within the wavelength range 290–350 nm.

were identified by reference to commercially available authentic standards. 7-Hydroxy-1,4-naphthoquinone was isolated by preparative HPLC and characterised on the basis of ^{1}H NMR [δ (ppm) in $CDCl_3$, 8.04 (1H, d, $J = 8.6$ Hz), 7.45 (1H, d, $J = 2.6$ Hz), 7.18 (1H, dd, $J = 8.6$ and 2.6 Hz)] and mass spectra ($m/z = 175$ $[M + H]^+$, 203 $[M + 29]^+$, 215 $[M + 41]^+$). Traces of naphthol were also found. Since carbamates and aryl esters are known to undergo photo-Fries reactions [9–14], we looked for photo-Fries rearrangement products, but did not find them.

For comparison, carbaryl was also irradiated in acetonitrile and methanol. The quantum yield of photolysis was evaluated as $(4.1 \pm 0.2) \times 10^{-3}$ and $(3.7 \pm 0.2) \times 10^{-3}$, respectively and 1-naphthol was found as the main photoproduct accounting for 37 and 65% of converted carbaryl, respectively.

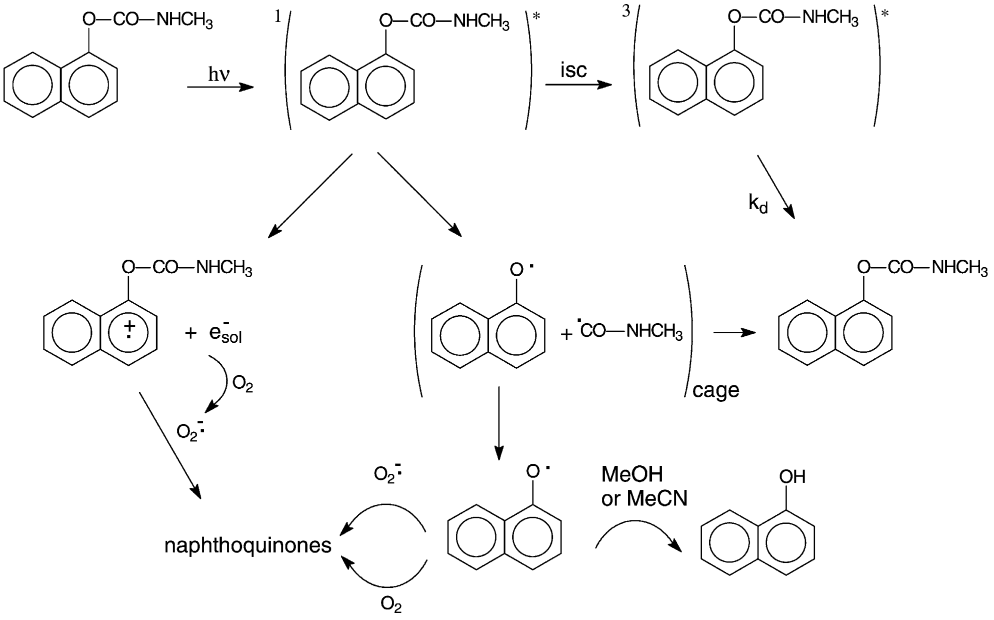
4. Discussion

Carbamates and aryl esters were reported to undergo photo-Fries rearrangement. This latter reaction that has been extensively studied ([13] and references therein) is believed to involve homolytic cleavage of the carbon–oxygen bond yielding a pair of radicals that further recombine to form rearrangement products. By coupling quenching experiments with CIDNP studies, Gritsan et al. brought evidence that the decomposition of naphthyl acetate into acetyl and naphthoxyl radicals occurs mostly via the singlet excited state [13]. In contrast, carbaryl is photooxidised into naphthoquinones and hydroxynaphthoquinones in water and mostly photoconverted into 1-naphthol in methanol and acetonitrile.

By monitoring the fluorescence decay, we found that the singlet excited state of carbaryl in water shows a lifetime of 33 ns, in line with those of naphthalene derivatives [16]. Laser-flash photolysis studies on aqueous carbaryl indicated that the singlet excited state intersystem crosses the triplet excited state. At the maximum of the T–T absorption band we measured: $\varepsilon \times \phi_{isc} = 3700 \pm 300\,M^{-1}\,cm^{-1}$. If we use the value measured in the case of 1-naphtyl acetate ($10^4\,M^{-1}\,cm^{-1}$ at 410 nm) as the molar extinction coefficient, we get $\phi_{isc} = 0.37$ for carbaryl. This latter value is very close to those measured for 1-naphthyl acetate (0.40 and 0.35 in acetonitrile and methanol, respectively [13]). To get a better insight into the role of the triplet state in the transformation, we tried to measure the quantum yield of carbaryl disappearance in nitrogen-saturated medium. Due to its high volatility, we could not get accurate values. However, we found data that did not significantly differ from those obtained in air-saturated medium. It seems therefore that the presence of oxygen does not influence the rate of carbaryl loss. It can be concluded that carbaryl does not react via the triplet excited state.

By photolysing aqueous carbaryl, we detected naphthoxyl radicals. It demontrates that the homolytic cleavage of the carbon–oxygen bond occurs. The naphthoxyl radicals observed are likely to be those escaping the cage after bond dissociation. In the case of 1-naphthyl acetate, naphthoxyl radicals were also detected [13]. In the two systems, yields of naphthoxyl radicals formation were found to be within the range 0.01–0.02.

The laser-flash study reveals that the primary steps in photolyses of carbaryl and 1-naphtyl acetate show several analogies. It means that carbaryl decomposes into *N*-methyl carbamyl and naphthoxyl radicals. The non-formation of photo-Fries rearrangement products and the very low quantum yield of carbaryl photolysis compared to that of 1-naphtyl acetate (about 100 times smaller) may indicate



Scheme 1.

that the in-cage recombination of *N*-methyl carbamyl and naphthoxyl radicals gives mostly carbaryl back. This specific recombination of radicals that is observed regardless the solvent is not explained.

Oxidation of carbaryl into naphthoquinones is likely to be subsequent to photoionisation that was shown to occur in water. In the presence of oxygen, solvated electrons should be transformed into superoxide anions that can recombine either with radical cations or with 1-naphthoxyl radicals. Both reactions are expected to finally produce naphthoquinones. Alternatively, 1-naphthoxyl radicals may react with oxygen to yield naphthoquinone after reduction. Oxidation was found to be a very minor pathway in solvents such as acetonitrile and methanol. Instead the main reaction path is the formation of 1-naphthol that may arise by H-atom transfer from solvent to naphthoxyl radical escaping the cage. Hydroxy-1,4-naphthoquinones are likely to be secondary photoproducts arising from 1,4-naphthoquinone [17]. The proposed mechanism for the reaction of carbaryl is depictured in Scheme 1.

In conclusion, we show that aqueous carbaryl exhibits a photochemical behaviour that contrasts with those of carbamates and aryl esters: oxidation occurs instead of photo-Fries rearrangement. Study of primary steps by laser-flash photolysis indicates that carbaryl populates its triplet state, but this latter seems unreactive. Scission of the oxygen–carbon bond takes place as demonstrated by the naphthoxyl radicals production. However, this pathway does not lead photo-Fries products. The oxidation of carbaryl is likely to involve naphthoxyl radicals escaping the cage and solvated electrons and radical cations produced in the photoionisation process.

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