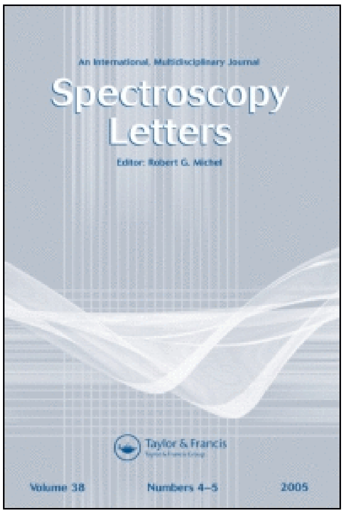

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Yaser A. Yousef[a]; Fayez El-Khatib[b]
[a] Chemistry Department, Yarmouk University, Irbid, Jordan [b] Chemistry Department, Jerash University, Jerash, Jordan

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Photodegradation of Carbaryl in Acetonitrile Solution

Yaser A. Yousef
Chemistry Department, Yarmouk University, Irbid, Jordan

Fayez El-Khatib
Chemistry Department, Jerash University, Jerash, Jordan

Abstract: The photochemical decomposition, induced by UV radiation, of the carbamate pesticide (Carbaryl) in acetonitrile has been examined by means of gas chromatography–Mass spectrometry (GC-MS). The result of continuous irradiation was almost total degradation of the pesticide examined. In order to investigate the nature of the reaction products, a spectroscopic study (UV-Vis, steady-state fluorescence, and fluorescence lifetime) of the products was performed. Phthalic anhydride and traces of 1,4-naphtalenedione as an intermediate were detected as reaction products. The presence of a trace amount of 1-naphthol as one of the photoproducts was confirmed by fluorescence lifetime measurements.

Keywords: Carbaryl, fluorescence, GC-MS, photodegradation, single photon counting

INTRODUCTION

Carbaryl (1-naphtyl *N*-methylcarbamate) was first synthesized in 1953 (Scheme 1), and in 1958, the Union Carbide Corporation began its commercial production.[1] It is produced by the reaction of 1-naphthol with methylisocyanate.[2]

Carbaryl is widely used in many countries as a broad-spectrum contact and ingestion insecticide with some systemic properties and controls a wide range of insect pests on crops.[3] It is used to control thrips, leaf hoppers,

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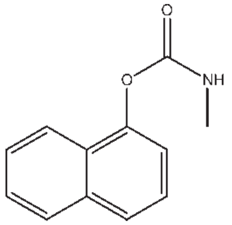
Address correspondence to Yaser A. Yousef, Chemistry Department, Yarmouk University, Irbid, Jordan. E-mail: yhaj@yu.edu.jo



Scheme 1. 1-Naphtyl *N*-methylcarbamate.

apple twinge borer, apple fruit worm, bugs, leaf miner, and other insects on citrus, vegetables, corn, and ornamentals. Initially, the principal nonbiological degradation pathway of Carbaryl in water involves base-catalyzed hydrolysis to 1-naphthol.[4] The photochemistry of Carbaryl was studied by Addison et al. in aerated and pure ethanol, cyclohexane, isopropyl alcohol, and *tert*-butanol. Irradiation of Carbaryl produced 1-naphthol and small amounts of naphthamides, naphthalene, and β-napthyl-1-naphthol.[5] In cyclohexane, 1-naphthol was the only decomposition product. Deuel et al. studied the photodecomposition of Carbaryl in deionized water. They confirmed that Carbaryl could be photodecomposed in an aqueous environment.[6] Carbaryl is used in the Jordanian agricultural valley where harsh weather conditions are known to exist. The daily average sunshine duration in that area is 9.1 hr, and clear sky conditions exist most of the year. Although Carbaryl is known to be stable towards solar radiation, the tail of its UV absorption ranges between 300 and 340 nm which falls within the solar spectrum in that area.[7] Therefore, focusing on the effect of UV light on Carbaryl can be considered an important agricultural and environmental issue. The photodegradation of Carbaryl in acetonitrile solution has not been investigated although acetonitrile is commonly used as part of the mobile phase for the separation of pesticides by high performance liquid chromotography (HPLC) technique. The identification of the photoproducts is also important because they could be potential pollutants to soil. In this work the photodegradation of carbaryl in acetonitrile solution is presented. For this purpose, gas chromatography–mass spectrometry (GC-MS) and several spectrophotometric techniques, UV absorption, fluorescence, and fluorescence lifetime spectrometries, were used as monitoring tools for the photodegradation process.

MATERIALS AND METHODS

Chemicals

Spectroscopic grade acetonitrile purchased from Aldrich Company (Madison, WI, USA) was used as received. No emission was detected when solvent is excited between 280 and 500 nm. Solid Carbaryl was a gift by a local pesticides production company MOBEDCO (Amman, Jordan). Excitation spectra were used for determining the purity of the fluorescent compounds.

Instrumentation

A Rayonet Photochemical reactor model RPR-100 (The Southern New England Ultraviolet Company, CT, USA) was used for the irradation. The unit contains a set of 15 lamps emitting at a maximum wavelength of 300 nm. A cooling fan is used to prevent thermal effects on the sample. GC-MS measurements were performed by using a GC model 7100 (HP) coupled to a VG 7070E E/B (Vacuum Generators, UK) sector field mass spectrometer. The system control and acquisition data station, originally supplied with the instrument, was upgraded by a new hardware and PC software from MSS Company. The software includes a mass spectral data library from NIST for automatic comparison of sample spectra with a standard. The following conditions were used: sample volume, 20 μl, column, 15 m; capillary, 0.5-mm i.d and 0.25-mm stationary phase film thickness; injector temperature, 250°C; initial oven temperature 70°C; waiting time, 2 min; rate, 15°C/min; final temperature, 300°C; mass range, 20–400 amu; scan rate, 15 amu/s; ionization method, EI; ion source temperature, 250°C; ionization energy, 70 eV; trap current, 100 μA. NIST mass data library was used for the identification of the mass spectral results. A Labomed Model Dual-PC was used to record the UV-Vis spectra operating at a medium speed of scanning. All fluorescence measurements were performed using a home-assembled fluorimeter.[8,9] A block diagram for its different components is shown in Fig. 1. It consists mainly of an air-cooled 450-W Xe lamp as the excitation light source (1), a 15-cm focal length excitation monochromator (2), 5-cm^3 quartz cell holder (3), 50-cm focal length spectrograph (4), a two-dimensional coupled charge detector (CCD) camera with 1024 × 376 pixels (5), detector controller (6), monochromator drive (7), and detector cooling (8). The CCD has an extended wavelength spectral response down to 200 nm by coating the front area with a layer of UV to visible converter. The detector is equipped with an electromechanical shutter to control the duration of light exposure and hence protect it from saturation. A spectrum with 150-nm width can be obtained in a time period as short as a few milliseconds by electronically scanning the detector while the spectrograph grating is fixed in place.

RESULTS AND DISCUSSION

The absorption spectrum for a fresh sample of Carbaryl in acetonitrile solvent showed the presence of a wide absorption band peaking at

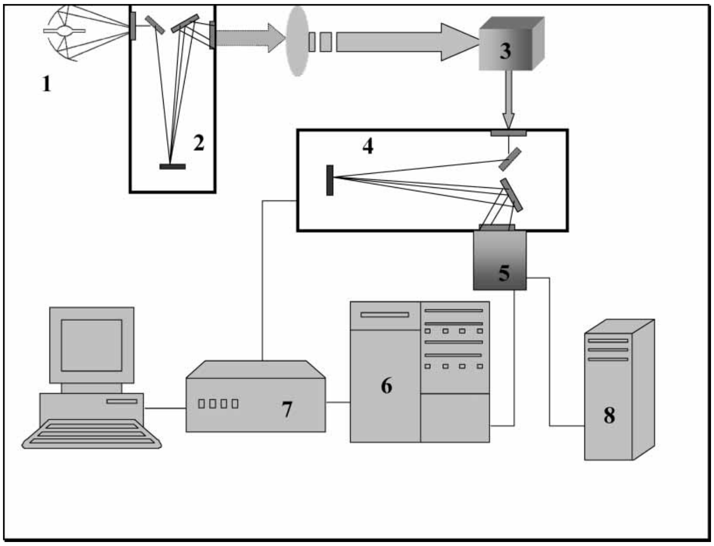


Figure 1. A block diagram for the home assembled OMA(IV) fluorometer.

280 nm (Fig. 2). Photolysis of solution by a Rayonet photochemical reactor UV leads to a different absorption spectrum, indicating the photochemical instability of the solution. For further confirmation, fresh and photodegraded samples were analyzed by other techniques such as fluorescence

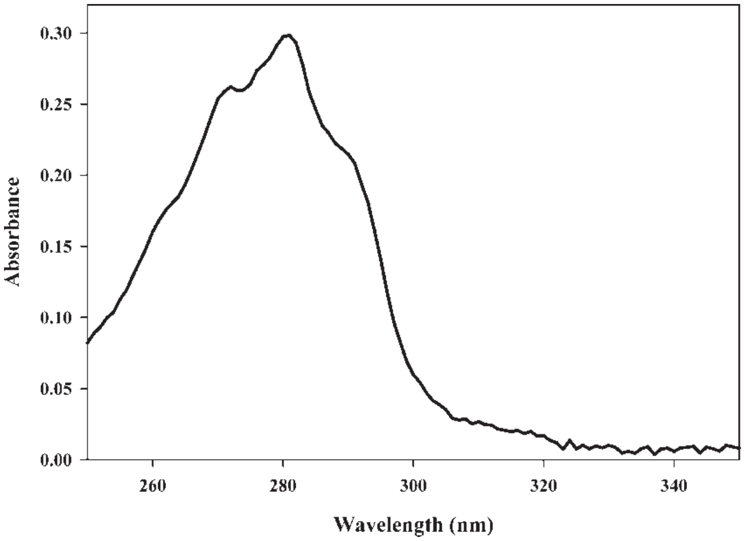
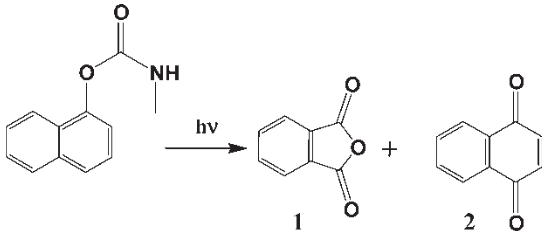


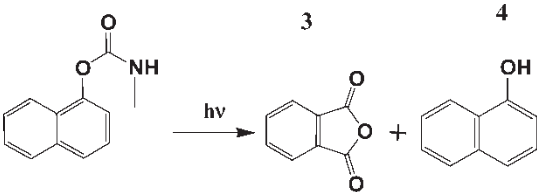
Figure 2. UV spectrum of 1 mM solution of Carbaryl in acetonitrile at 25°C.

emission, fluorescence lifetime, and mass spectrometry. The primary effect of ultraviolet light radiation (UVR) seems to be cleavage of the ester bond, but other modifications in the Carbaryl molecule also occur.[10] To our knowledge, photodegradation of Carbaryl in acetonitrile solvent has not been described in the literature. For this purpose, a solution of 5 mL of Carbaryl in acetonitrile was injected into the GC-MS yielding a single chromatographic peak with a retention time of 8.15 min. Mass analysis of this peak showed the mass spectrum of Carbaryl by direct comparison with the spectrum in the NIST database. An aliquot of the same solution was irradiated in the Rayonet photochemical reactor for 1 hr and analyzed using the same temperature program in the GC-MS. The resulting chromatogram showed the presence of three major peaks: the first after 3.5 min with a mass spectrum identical to phthalic anhydride; the second peak after 4.4 min with a mass spectrum similar to 1,4-naphthalene dione; the third peak was at 8.15 min corresponding with the undegraded Carbaryl. The photodegraded solution was irradiated for 2 more hours and analyzed similarly. In this case, the chromatogram showed the presence of three peaks: the first after 3.5 min with a mass spectrum identical to phthalic anhydride; the second minor peak after 5.5 min with a mass spectrum indicating the formation of 1-naphthol; the third peak was at 8.15 min corresponding with the undegraded Carbaryl. The photodegraded solution was further irradiated for 2 more hours where complete photodegradation was obtained, as confirmed by the disappearance of the peak at 8.15 min corresponding with the starting material. In this chromatogram two peaks were found, the first corresponding with phthalic anhydride and the second indicating the presence of trace amount of 1-naphthol. The photodegradation of Carbaryl in aqueous solution was previously investigated, and the final photoproduct was found to be phthalic acid.[11] The current study showed the formation of phthalic anhydride as the final photoproduct. The reaction mechanism for photodegradation is shown in Schemes 2 and 3.

The fluorescence spectra for pure and photodegraded Carbaryl in acetonitrile are shown in Fig. 3. It is clear that UV photolysis causes a red shift



Scheme 2. Photolysis for 1 hr yielded the formation of phthalic anhydride (1) and 1,4-naphthalene dione (2).



Scheme 3. Photolysis for 3 or 5 hr yielded the formation of phthalic anhydride (3) and traces of 1-naphthol (4).

in the fluorescence peak. To confirm the formation of 1-naphthol as one of the photoproducts, which was found to exist in trace amounts, the fluorescence lifetime of fresh and photolyzed Carbaryl were measured using single photon counting technique. To our knowledge, the fluorescence decay time has not been in the literature. The decay, shown in Fig. 4, was found to follow a single exponential of 12.8 ns for a fresh solution of the pesticide in acetonitrile. The dotted curve with fast decay shows the lamp and system response time profile. The dotted curve with slow

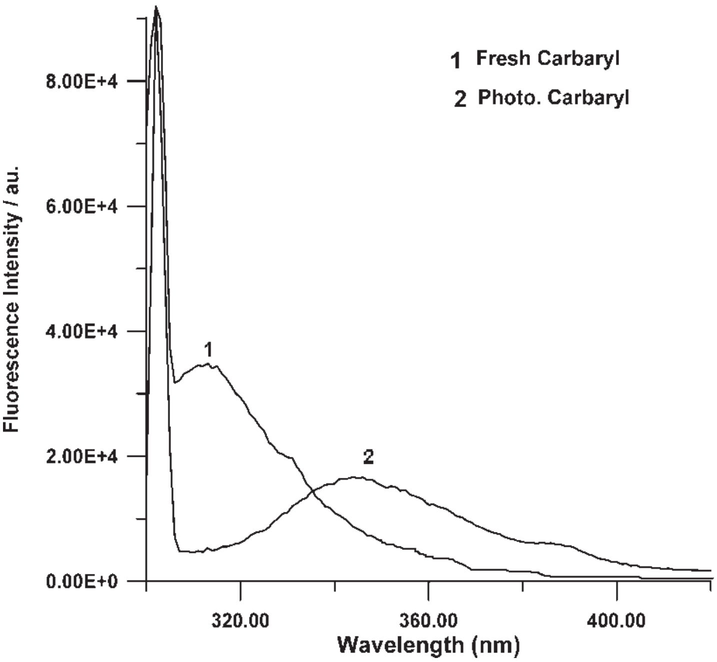


Figure 3. Fluorescence spectra of fresh and photolyzed (red-shifted) Carbaryl in acetonitrile solvent.

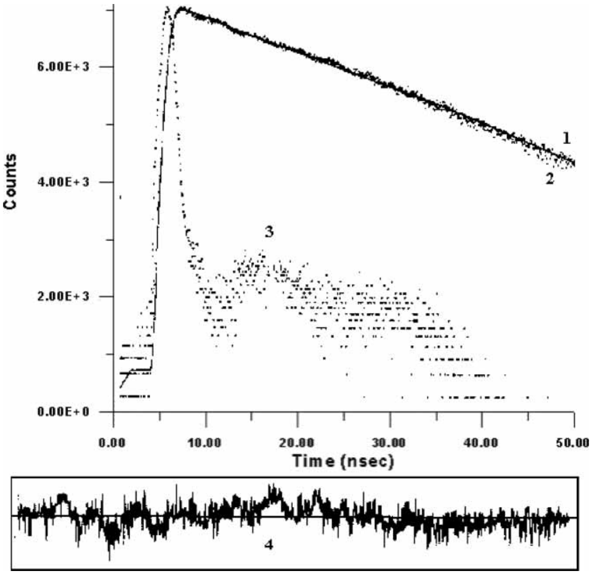


Figure 4. Fluorescence decay time of fresh Carbaryl in acetonitrile solvent. Dotted fast decay line is lamp profile, while the slow decay is the combined lamp and sample profile. Solid line is the fitting profile.

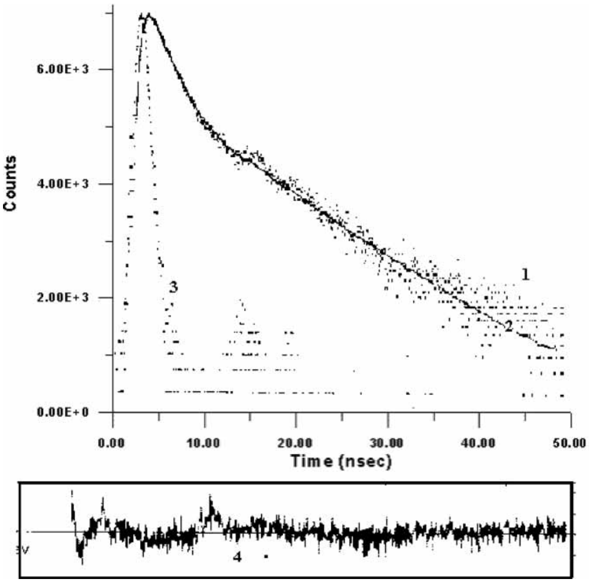


Figure 5. Fluorescence decay time of photolyzed Carbaryl in acetonitrile solvent. Dotted fast decay line is lamp profile, while the slow decay is the combined lamp and sample profile. Solid line is the fitting profile.

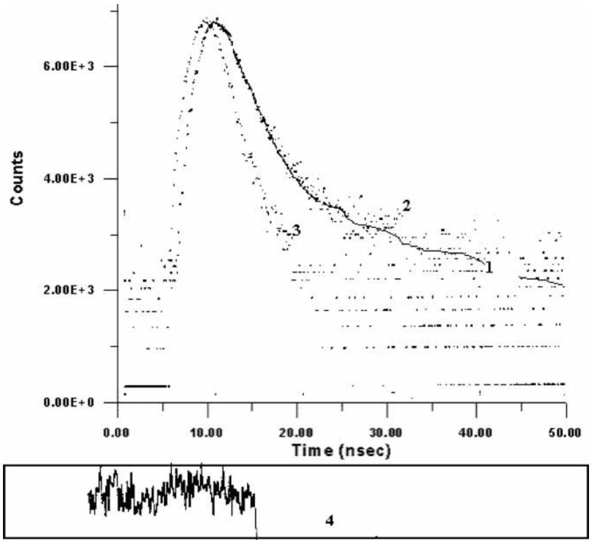


Figure 6. Fluorescence decay time of photolyzed Carbaryl in acetonitrile solvent. Dotted fast decay line is lamp profile, while the other decay is the combined lamp and sample profile. Solid line is the fitting profile.

decay is the combined lamp and sample profile. The solid line is the fitting profile calculated using special deconvolution software supplied by Edinburgh Instruments (Scotland, UK). Figure 5 shows the fluorescence decay for Carbaryl after 4 hr of photolysis. The decay could be fitted to double exponential decay with a fast decay component of 0.9 ns and a relatively slow component of 7.9 ns. The contribution of the fast decay component is 85%. Photolysis for longer periods caused the complete disappearance of the slow decay component. Figure 6 shows the presence of only single fast exponential decay of 0.7 ns. To confirm the presence of 1-naphthol as one of the photoproducts, the fluorescence decay time for a pure sample of 1-naphthol in acetonitrile was measured. The decay could be fitted to single exponential with a lifetime of 7.8 ns as shown in Fig. 7. This result agrees with the GC-MS analysis and provides conclusive evidence for the formation of 1-naphthol as a photoproduct.

CONCLUSIONS

Carbaryl undergoes photodegradation in both aqueous and acetonitrile solvents. The degradation pathway is dependent on the type of solvent. The final photoproducts in acetonitrile solution are different from those reported in aqueous medium. The fluorescence lifetime for Carbaryl and 1-naphthol

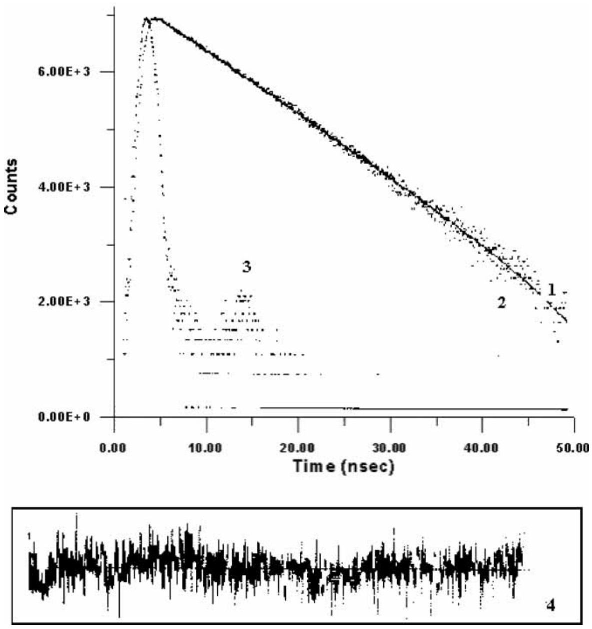


Figure 7. Fluorescence decay time of fresh 1-naphthol in acetonitrile solvent. Dotted fast decay line is lamp profile, while the other decay is the combined lamp and sample profile. Solid line is the fitting profile.

is reported and used for identification purposes. Fluorescence and fluorescence lifetime techniques are used as complementary tools to GC-MS for monitoring the photodegradation mechanism.

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