Journal of Photochemistry and Photobiology A: Chemistry 235 (2012) 1–6

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

A density functional theory and laser flash photolysis investigation of carbofuran photodegradation in aqueous medium

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ARTICLE INFO

Article history:
Received 22 August 2011
Received in revised form 14 February 2012
Accepted 17 February 2012
Available online 8 March 2012

Keywords:
DFT
Photodegradation
Carbofuran
BDE
Laser flash photolysis
Homolysis

ABSTRACT

Density functional theory (DFT) approach was used to study the photodegradation of Carbofuran in aqueous medium. This computational method enables us to assign the electronic transitions and interpret the dissociative behavior upon irradiation based on a thermodynamical analysis of the bond dissociation energies (BDE) of Carbofuran. According to these calculations, phenoxy C—O bond appears weaker than the C—N bonds. Hence, it was predicted that the photodegradation of Carbofuran should occur with an initial homolytic dissociation of the C—O bond of the carbamate moiety. Laser Flash Photolysis (LFP) results clearly indicate the formation of the phenoxyl radical, which support the outcome of this theoretical approach.

1. Introduction

Carbofuran (2,3-dihydro-2,2-dimethyl benzofuran-7-yl methyl carbamate) is a broad spectrum insecticide, nematicide and miticide [1]. Residual fate of Carbofuran has been extensively investigated in water, soil and in different experimental conditions [2–5]. In fact, several pathways were suggested for Carbofuran photodegradation, and the major observed photoproduct was phenol derivative [6]. Chiron et al. have published a report on Carbofuran photodegradation where two decomposition products were identified by LC–MS, 3-hydroxy-7-carbofuranphenol as a product of hydrolysis and 2-hydroxy-3-(2-methylprop-1-enyl)-phenyl-N-methylcarbamate arising from a rearrangement product [7]. John and Howard have proposed a mechanism for the first steps of the Carbofuran photodegradation in water. According to these authors, the carbamate group undergoes a cleavage process via C—O heterolysis, leading to the formation of carbamic acid and 2,3-dihydro-2,2dimethylbenzofuran-7-ol [8]. However, the knowledge of the main photochemical reaction remains incomplete, and the mechanistic data are still needed. A mechanism of similar system is shown in Fig. 1 [9]. Upon irradiation, the generated excited singlet may undergo intersystem crossing (ISC) from S_1 to T_1, homolytic cleavage to form radical pair or heterolytic cleavage to form ion pair. The initially formed radical pair may be converted to the more stable (in polar solvents) ion pair by electron transfer (ET). Finally, both radical pairs and ion pairs may lead to formation of the starting substrate, namely carbofuran, within a cage recombination process: Radical Combination (RCom) or Ion Combination (ICom).

On the other hand, quantum chemical computations have recently been considered as an effective tool for the analysis of pesticide molecules [10–15]. Arul Dhas et al. have performed the density functional theory (DFT) computations to interpret electronic and vibrational spectra, and intramolecular charge transfer responsible for biological activity of Chlorothalonil [16]. Aaron and al. have applied a theoretical, gradient-corrected Hartree–Fock density functional theory (HF-DFT) approach to determine the bond dissociation energy (BDE) for the photodegradation processes of the 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide in the gas phase and in aqueous medium [17].

In this context, the present work examines the mechanistic aspect of the first step of Carbofuran photochemical degradation in water, based on a theoretical approach using the DFT methods. In addition, our experimental data given by laser flash photolysis permit to corroborate this theoretical approach.

2. Materials and methods

2.1. Experimental

The compound Carbofuran (98) was purchased from Sigma–Aldrich. UV–vis spectrum was taken for aqueous

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doi:10.1016/j.jphotochem.2012.02.018

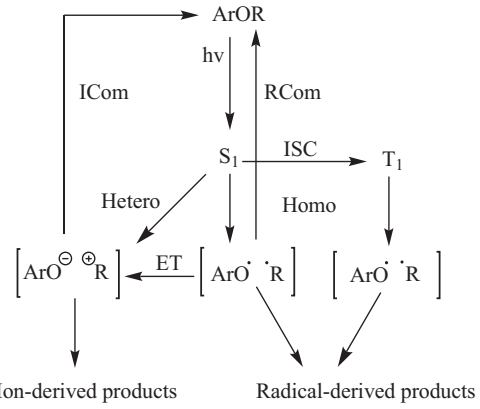

Fig. 1. General mechanism of photodissociation.

sample of Carbofuran (0.1 mM), using the HP-8452A photo-diode array spectrometer in the region 190–700 nm.

Laser flash photolysis (LFP): Transient absorption experiments in the 20 ns to 500 μs time scale were carried out on a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS.60). Excitation (λ = 266 nm) was from the fourth harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser (pulse width 5 ns), and was used in a right-angle geometry with respect to the monitoring light beam. A 3 cm^3 volume of an argon-saturated solution was used in a quartz cell, and was stirred after each flash irradiation. Individual cell samples were used for a maximum of 10 consecutive experiments. The laser energy was within the range 1–15 mJ. The obtained signal was an average of about 10 shots. The transient absorbance at preselected wavelength was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator, and a 1P28 photomultiplier. A spectrometer control unit was used for synchronizing the pulsed light source and programmable shutters with the laser output. This also housed the high-voltage power supply for the photomultiplier. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyze the digitized signal.

LC/MS studies were carried out with a Waters (Alliance 2695) high performance liquid chromatography system coupled to a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with a pneumatically assisted electrospray ionization source (ESI) and a Waters photodiode array detector. Data acquisition and processing were performed by MassLynx NT 3.5 system. Chromatography was run using a Nucleodur column100-5 C8 ec (250 × 4.6 mm, 5 μm) and a 60/40 (v/v) mixture of acetonitrile and water with 0.2% acetic acid as mobile phase at 1 mL min^{-1}. The electrospray source parameters were:capillary voltage 3.5 kV (or 3 kV in the negative mode), cone voltage 15 V, source block temperature 120 °C, desolvatation gas temperature 400 °C. Argon was used for collisional activated dissociation (CAD) at a pressure of 1.5×10^{-3} torr and 10–50 eV collision energy.

The irradiations at 254 nm were obtained with PHILIPS TUV 6 W lamp delivering a parallel beam.

2.2. Computational details

The computation was performed using two density functional theory (DFT) based methodologies. The first methodology is based on the combination of the Beckes three-parameter adiabatic connection exchange functional (B3) with the Lee–Yang–Parr (LYP) correlation functional (B3LYP method) [18,19]. The second DFT methodology, based on PBE1 exchange functional combined with the PBE correlation one10 (PBE0 method) is characterized by certain further improvements over the other DFT functional methods [20]. Indeed, generally the later methods are constructed with the main aim of improving the well-known deficiency in their long-range behavior. Both of the employed computational methodologies can be considered as hybrid HF-DFT (i.e. they include an admixture of HF exchange energy), in contrast to the pure DFT ones. The standard Pople-type 6-311++G(d,p) basis set was employed for orbital expansion, solving the Kohn-Sham (KS) SCF equations iteratively for each particular purpose of this study.

Electronic transitions for the molecule were calculated from excited state calculations using the time dependent-density functional theory (TD-DFT) method. This method is frequently found to be a powerful and accurate approach for describing low-lying excited states of conjugated molecules and has consequently been applied to solve many chemical and physical problems [21–24].

The influence of the solvent on the energetics of bond dissociation processes for the species under study was accounted for in the framework of the self- consistent reaction field (SCRF) methodology, employing the Polarized Continuum Model (PCM) for water, the later medium being treated as a continuous dielectric with a relative dielectric constant (=78.39) [24–26]. In general, the PCM calculations were based on the gas-phase structures optimized at the same theoretical level. Such method is used in many other works and is known to be consistent to study similar systems [27,28].

Subsequently, after locating the stationary points on the potential energy surfaces (PESs) under study, their character was tested by computing the harmonic vibrational frequencies. The absence of imaginary frequencies (namely negative eigenvalues of the second-derivative matrix) was used as a criterion that a particular point on the PES corresponded to a minimum energy structure (instead of being a saddle point). Thermochemistry of the bond dissociation processes was analyzed in the following way, described below.

The energies for each of the involved species were corrected by the zero-point vibrational energies, computed on the basis of harmonic vibrational analysis. Subsequently, the rotational, vibrational and translational contributions were added to the obtained $E(0)$ values, in order to get the $E(T)$ ones (for $T = 298.15$ K). All of these contributions were calculated on the basis of standard statistical mechanics expressions for an ideal gas constituted of harmonic oscillators within a canonical ensemble [29]. The corresponding enthalpies $H(T)$ and free enthalpies $G(T)$ were calculated from Eqs. (1) and (2):

$$H(T) = E(T) + RT \tag{1}$$

$$G(T) = H(T) - TS \tag{2}$$

Finally, the bond dissociation reaction energies E and enthalpies H were calculated from the standard expressions for the corresponding quantities, given in Eqs. (3)–(5):

$$\Delta E^0 = \sum_p Ep - \sum_r Er \tag{3}$$

$$\Delta H^0 = \sum_p Hp - \sum_r Hr \tag{4}$$

$$\Delta G^0 = \sum_p Gp - \sum_r Gr \tag{5}$$

where the indices p and r represent, respectively, the products and the reactants of the processes under study.

All quantum chemical calculations for the purpose of the present study were carried out with the Gaussian 09 series.