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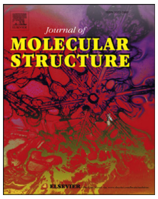

UV laser-induced photolysis of matrix isolated *o*-guaiacol

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ABSTRACT

A matrix isolation study of structure and infrared spectra of *o*-guaiacol (*o*-methoxyphenol, GU) has been performed showing that the most stable conformer of the compound is present in argon and xenon matrices. Photochemical reactions of *o*-guaiacol were induced using UV-laser radiation and followed by the FTIR spectroscopy. Four photolysis pathways have been considered based on the positions of new bands appearing during irradiation of the matrices. It was concluded that the cleavage of the O—H bond is an initial step of the reactions and a number of photoproducts have been identified originating from the subsequent ring opening and decarbonylation processes as well as the O—CH_3 bond cleavage. Among the photoproducts are cyclopetadienone and long-chain ketenes with conjugated/cumulated C=O and C=C bonds.

1. Introduction

The phenolic compounds play an essential role in plants acting as very efficient antioxidant and radical-scavenging agents as well as UV absorbers. Some of them are also widely used in medical and dental practices due to their analgesic, anti-inflammatory and anesthetic properties [1–8]. Due to the increasing bacterial resistance to antibiotics, compounds with the natural origin isolated from plants, algae, and microorganisms, such as plant phenols may serve as model template for the production of new antimicrobial agents [9].

The title compound *o*-guaiacol (*o*-methoxyphenol) (see Scheme 1) is of natural origin, often derived from lignin. Guaiacol is present in smoke that results from pyrolysis of wood lignin [10,11]. It appears in troposphere as lignocellulosic biomass burning pollutant and is regarded as one of the precursors of secondary organic aerosols [12,13]. *o*-Guaiacol as well as its two isomers are often used as a model compound in studies of decomposition and recombination mechanisms of lignin [10]. This compound contributes to the flavor of many food products [14–18] such as roasted coffee [19] or whiskey [20]. Guaiacol is also used in manufacture of various fragrances e.g. eugenol and vanilline [21].

Complexes of guaiacol with various H-acceptor solvents has been extensively studied (see for example [22]). Self-association of guaiacol and its complexation with nitrogen and carbon monoxide, mostly in the OH stretching region were investigated under cryogenic matrix conditions [23,24]. More recently, high resolution electronic spectra in a molecular beam together with *ab initio* calculations have been used to elucidate a structure of the guaiacol both in ground and S_1 excited states [25]. The IR/UV and UV/UV double resonance study of the guaiacol dimers in pulsed supersonic expansions was reported. It was shown that guaiacol was present in one conformation and the dimers were attached by the O—H···O hydrogen bonds between the OH groups [26].

Scheer et al. studied the pyrolysis of the guaiacols and detected the decomposition products by both matrix isolation infrared spectroscopy and photoionization *time-of-flight* mass spectrometry [10,27]. Using combination of gas phase and ultrafast solution spectroscopies Greenough et al. [28] demonstrated for *o*-guaiacol that it was possible to track conformer specific photodissociation dynamics in solution through solvent choice. Very recently, Priya and Lakshmipathi followed the mechanism of atmospherically important reactions of guaiacol with OH radical [29].

The goal of the present work is to find out what are the photolysis pathways of *o*-guaiacol isolated in low temperature argon and xenon matrices using tunable UV radiation source. For our experimental studies we chose matrix isolation coupled with FTIR spectroscopy since it is especially powerful technique for

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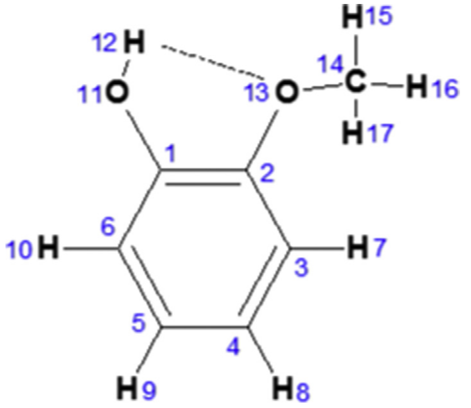

Scheme 1. Schematic representation of GU molecule with the adopted numbering of atoms.

detection and identification of phototransformations products [30–41]. Interpretation of the experimental results was supported by B3LYP/6–311++G(2d,2p) calculations.

2. Experimental

2.1. Matrix isolation studies

In order to prepare low-temperature argon or xenon matrices, a liquid sample of guaiacol (supplied by Aldrich, purity>98%) was evaporated from a small bulb held at 0–5 °C located outside the cryostat chamber. The vapors of GU were then deposited with a large excess of the matrix gas (Ar or Xe) onto a CsI window cooled to 15 K and 50 K for Ar and Xe, respectively. All experiments were performed using an APD Cryogenics (ARS-2HW) close-cycle helium refrigeration system. Infrared spectra (4000–400 cm^{-1}, 0.5 cm^{-1} resolution) were collected in the transmission mode at 11 K by means of a Bruker IFS 66 FTIR spectrometer, equipped with a liquid N_2 cooled MCT detector.

2.2. Photolysis experiment

The matrices GU/Ar and GU/Xe were irradiated with the tunable UV light provided by the frequency doubled signal beam of a pulsed (7 ns) optical parametric oscillator Vibrant 355 (Opotek Inc.) (repetition rate 10 Hz) pumped with a pulsed Nd:YAG laser (Quantel). The average pulse energy was ~3.8 mJ.

2.3. Computational details

The quantum chemical calculations were performed with the Gaussian09-D.01 program package [42]. Structures of the minima and transition states as well as photolysis products in the ground state S_0 were optimized at the B3LYP/6–311++G(2d,2p) level [43–45]. The associated force constant matrices were calculated to evaluate harmonic wavenumbers and zero-point vibrational (ZPE) corrections. The DFT wavenumbers were scaled down to account for anharmonicity effects by 0.984 above 2500 cm^{-1}, and by 0.944 for the 2500-400 cm^{-1} spectral region. Potential energy distributions (PED) of the normal modes were computed with the GAR2-PED program [46] and the vibrational spectra were simulated using SYNSPEC program [47].

3. Results and discussion

3.1. Geometry and energetics of the guaiacol conformers

The performed B3LYP calculations revealed three stable structures on the S_0 potential energy surface that differ in relative orientation of the hydroxy and methoxy groups. Therefore, GU molecule has three different conformers: *anti-syn* (GU1), *anti-anti* (GU2) and *gauche-anti* (GU3). Their structures are presented in the upper part of Fig. 1 and values of the key angles calculated for them at B3LYP/6–311++G(2d,2p) level are given in Table 1.

Two of the three conformers are characterized by C_s symmetry whereas in the third one (GU3) the CH_3 group of the methoxy moiety is tilted above the aromatic ring (C_1 symmetry). The most

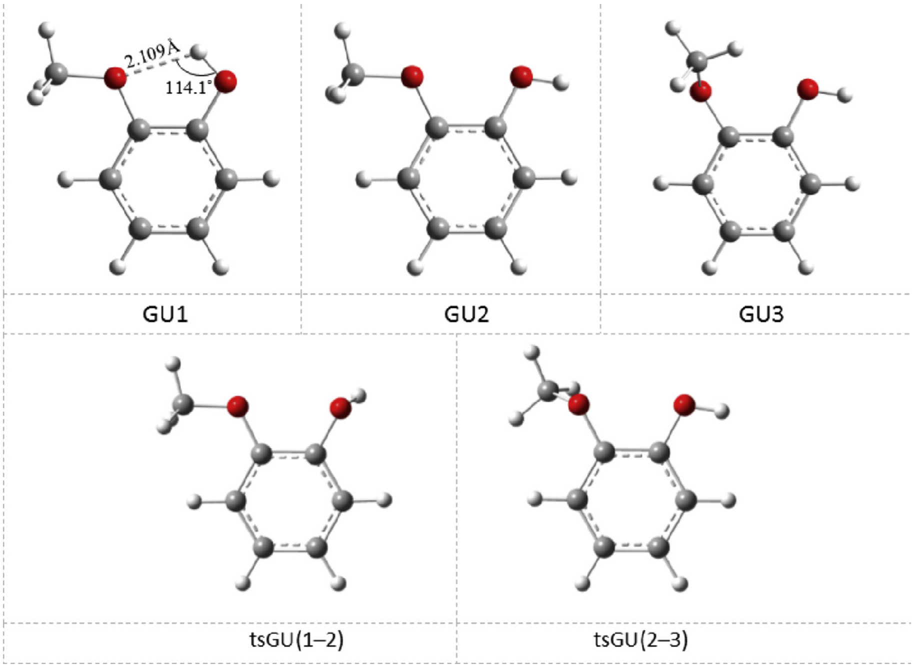

Fig. 1. The B3LYP/6–311++G(2d,2p) optimized structures of minima and transition states of guaiacol.

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