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A combined laser flash photolysis, density functional theory and atoms in molecules study of the photochemical hydrogen abstraction by pyrene-4,5-dione

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ABSTRACT

The photochemical hydrogen abstraction reaction of pyrene-4,5-dione (**3**) has been investigated by laser flash photolysis. Excitation ($\lambda = 355$ nm) of a degassed solution of **3** in acetonitrile resulted in the formation of a detectable transient with absorption maxima at 380 and 470 nm. This transient decays with a lifetime of around 4.8 μs and is quenched by oxygen. This transient is most probably a triplet state of **3**. Addition of hydrogen donors, such as 2-propanol; 1,4-cyclohexadiene or 4-methoxyphenol led to the formation of a new transient with λ_{max} at 380, 500 nm and a broad absorption at 640 nm. This new transient slowly decays with second order kinetics and was assigned to the semiquinone radical obtained from the hydrogen abstraction reaction. Using DFT and AIM calculations the reactivity of **3** and 9,10-phenanthrenequinone (**1**) is best interpreted as a proton coupled electron transfer like mechanism for the hydrogen abstraction from 2-propanol.

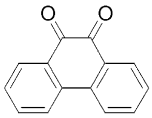
1. Introduction

It is known that *ortho*-quinones play important roles in photobiology [1–5]. The photochemistry of α-diketones (and the closely related *ortho*-quinones) has been a subject of interest for a long time and this field of investigation has continued to be very active [6]. Several *ortho*-quinones have been found to be photoreactive in the presence of hydrogen and electron donors [7–24].

The reactivity of aromatic ketones is dependent on the nature of their lowest triplet excited state, with the n,π* triplet being the reactive state [25]. Where the ketones have a lowest π,π* triplet state it has been accepted that they react predominantly via the higher energy n,π* state, populated thermally from the lower energy state [20,26,27]. The photoreactivity of 9,10-phenanthrenequinone (**1**) and other triplets [17,20] has been observed to be dependent upon the solvent polarity and is related to a small energy separation between the n,π* and π,π* triplet levels, thus leading to an inversion of the configuration. On the other hand, quinone **2** does not show an inversion of the triplet state, and is found to be π,π* in all solvents. As a result, **2** is less reactive than **1** towards hydrogen abstraction [17,19].

The irradiation of *ortho*-quinones in the presence of olefins leads to the formation of dihydrodioxins (DHDs) [6–8,12,28–30]. These adducts have been used as a photoactivated masking group for DNA cleavage [31]. Recently, Wilson and coworkers showed that for pyrene-4,5-dione dihydrodioxins the reaction is reversible with UV light, releasing pyrene-4,5-dione (**3**) [32].

This study reports the first results of the photochemical hydrogen abstraction reaction of **3** as investigated by laser flash photolysis irradiation. In addition, DFT and AIM calculations of the reactions of the triplet excited states of **1** and **3** with 2-propanol were performed.



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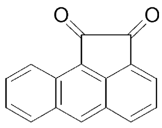

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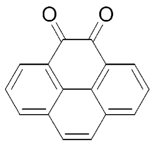

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2. Materials and methods

2.1. Materials

Solvents were UV grade. Pyrene-4,5-dione (**3**) was prepared according to a literature procedure and spectroscopic data were in

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accord with the reported results [33]. The quinone was recrystallized from acetonitrile from which crystals suitable for single crystal X-ray diffraction were obtained. Initial diffraction studies revealed an identical crystal system, space group and unit cell dimensions similar to those reported by Müellen [34]. 4-Methoxyphenol, 1,4-cyclohexadiene and β-carotene (Aldrich), were used as received.

2.2. *Laser flash photolysis*

The laser flash photolysis experiments were carried out on a LuzChem Instrument model mLFP122 either at the University of Ottawa, Canada, or at the Universidade Federal da Bahia, Brazil. Samples were contained in a 10 mm × 10 mm cell made from Suprasil tubing and were deaerated by bubbling with oxygen-free nitrogen for about 30 min. The samples were irradiated with a Nd/YAG Surelite laser, using the third harmonic ($\lambda = 355$ nm, ~4–6 ns, ≥40 mJ/pulse), with the signal being detected by a Tektronix TDS2012 oscilloscope. The concentration of **3** (~1 mM) was chosen in order to give an absorption at the wavelength of excitation (355 nm) of ~0.5.

2.3. *Low temperature phosphoresce*

The phosphorescence spectra in methylcyclohexane glass of **3** were recorded on a Time Resolved fluorometer from Edinburgh Analytical Instrument F900 in the phosphorescence mode which used a Xe pulsed lamp and a multichanel scaler.

2.4. *Computational methods*

The geometries were optimized using standard techniques [35], and after geometry optimization, vibrational analysis was performed and the resulting geometries were confirmed as true minima on the potential energy surface, as shown by the absence of imaginary frequencies. Geometrical, energetic and AIM calculations were performed at UB3LYP/6-311++G**//UB3LYP/6-31G* for all structures. Energy differences correspond to enthalpy differences at 298 K and 1 atm. All calculations were performed with the Gaussian 98 package of programs [36]. AIM (atoms in molecules) [37,38] calculations were performed on AIM 2000, v2.0. The AIM theory was used to investigate the interactions involved in the hydrogen abstraction reaction from the triplet state of **1** and **3**.

3. Results and discussion

3.1. *Laser flash photolysis*

Laser irradiation of a deoxygenated solution of **3** in acetonitrile resulted in the formation of a signal with maximum at 380 and 470 nm (Fig. 1). This transient decays by first order kinetics with a lifetime of around 4.8 μs and was quenched by oxygen (see insert Fig. 1). This decay is concentration dependent, reflecting self-quenching of the triplet. For acetonitrile we were able to measure a self-quenching rate constant of 3.1×10^8 L mol^{-1} s^{-1}. A similar value (2.0×10^8 L mol^{-1} s^{-1}) was found for the triplet of 9,10-phenanthrenequinone (**1**) in the same solvent [20]. The transient from irradiation of **3** is quenched by β-carotene (E_T = 21 kcal mol^{-1}) [39] with a diffusion controlled rate constant, leading to the formation of a 520 nm band characteristic of the β-carotene triplet.

Addition of 2-propanol, 1,4-cyclohexadiene or 4-methoxyphenol led to a shortening of the triplet lifetime of **3**. The triplet decay of this ketone followed pseudo-first-order kinetics in the presence of these quenchers, with the experimentally observed kinetic rate constant, k_{obs}, being related to the quenching rate constant, k_q, according to Eq. (1):

$$k_{obs} = k_0 + k_q[Q] \quad (1)$$

where k_0 is the decay rate constant of the triplet in the absence of the quencher, and [Q] is the quencher concentration. Plots based on this equation for the triplet of **3** being quenched by 2-propanol, 1,4-cyclohexadiene or 4-methoxyphenol were found to be linear, from which the value of k_q can be determined. Fig. 2 shows a representative quenching plot for 2-propanol and Table 1 details the rate constants.

The addition of 2-propanol to an acetonitrile solution of **3** leads to the formation of a new transient with λ_{max} around 380 and 500 nm and a broad absorption at 640 nm. Fig. 3 shows the transient absorption spectra recorded in neat 2-propanol. These spectra also show a strong bleaching signal centered at 415 nm, which is coincident with the maximum absorption for **3** in the ground-state. It is important to note that the triplet absorption spectrum for **3** in acetonitrile also shows a valley in the same region. Similar

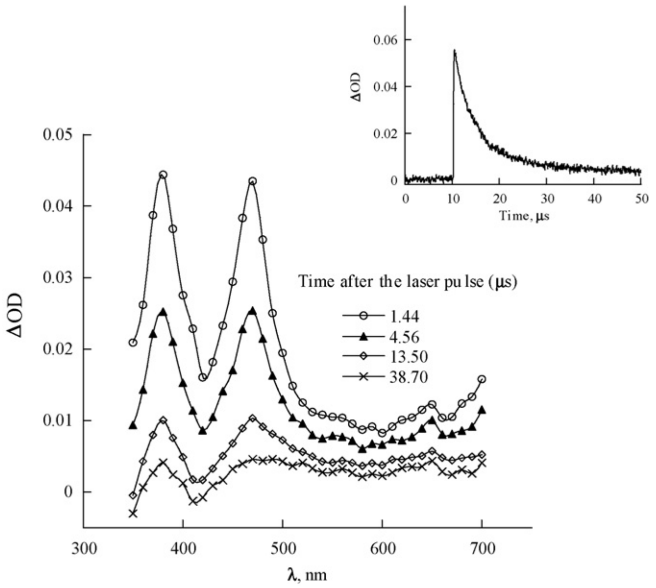

Fig. 1. Transient absorption spectra recorded after 355 nm laser excitation of **3** in acetonitrile solution. Insert: decay at 470 nm.

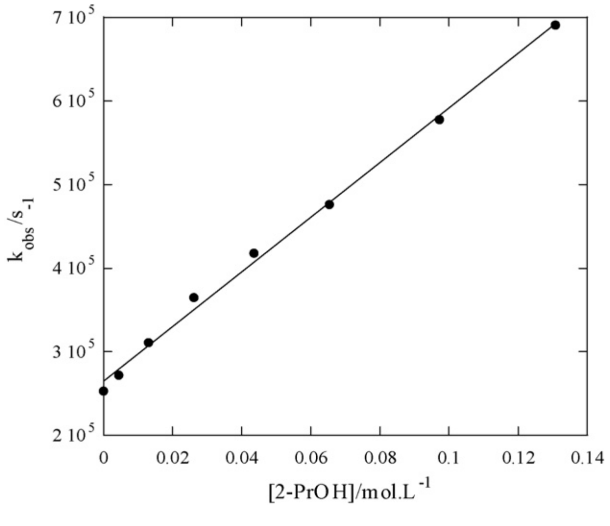

Fig. 2. Quenching plot for the triplet of **3** by 2-propanol in acetonitrile solution. λ_{exc} = 355 nm; λ_{mon} = 470 nm.