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From planes to bowls: photodissociation of the bisanthenequinone cation

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Abstract

We present a combined experimental and theoretical study of the photodissociation of the bisanthenequinone ($C_{28}H_{12}O_2$) cation, Bq^+ . The experiments show that, upon photolysis, the Bq^+ cation does not dehydrogenate, but instead fragments through the sequential loss of the two neutral carbonyl groups, causing the formation of five-membered carbon cycles. Quantum chemical calculations confirm this $Bq^+ \rightarrow [Bq - CO]^+ \rightarrow [Bq - 2CO]^+$ sequence as the energetically most favorable reaction pathway. For the first CO loss, a transition state with a barrier of ~ 3.2 eV is found, substantially lower than the lowest calculated H loss dissociation pathway (~ 4.9 eV). A similar situation applies for the second CO loss channel (~ 3.8 eV vs. ~ 4.7 eV), but where the first dissociation step does not strongly alter the planar PAH geometry, the second step transforms the molecule into a bowl-shaped one.

Keywords: Dissociation, Hydrocarbon molecules, Bisanthenquinone

1. Introduction

Bisanthenequinone (Bq) belongs to the family of the polycyclic aromatic hydrocarbon (PAH) quinones. These molecules are known products in the photo-oxidation of environmentally relevant PAHs (Alam et al., 2014; García, 1994). During incomplete combustion processes quinones are released into the atmosphere (Iinuma et al., 2007; Layshock et al., 2010; Valavanidis et al., 2006). They are also used in (in)organic synthesis, as oxidizing agent (March, 2005) or because of their pharmacological relevance (Patai, 1974; Liu, 2010). They may also be of astronomical relevance (Tielens, 2008), the motivation for the present study.

The vibrational signatures of PAHs dominate the mid-infrared spectra of many objects in space and are key contributors to the energy and ionization balance of the gas (Tielens, 2008). Interstellar PAHs are assumed to form in processes akin to soot formation in the cooling ejecta of carbon-rich Red Giant stars as they flow from the stellar photosphere into the interstellar medium (Frenklach and Feigelson, 1989; Cherchneff et al., 1992). Subsequently, they are further processed for millions of years by photons of the interstellar radiation field (Tielens, 2013). Driven by this astrophysical interest, experiments focusing on the photoexcitation of PAHs have attracted much interest in recent years (Zhen et al., 2014a, 2016). A number of different processes can take place, varying from sequential fragmentation (Ekern et al., 1998; West et al., 2012; Zhen et al., 2014a), isomerization (Dyakov et al., 2006; Johansson et al., 2011; Solano and Mayer, 2015; Simon et al., 2017; Trinquier et al., 2017) and ongoing ionization (Holm et al., 2011;

Zhen et al., 2015). Dedicated studies of the involved dissociation channels provide information on the molecular dynamics at play and this is interesting, both from an astronomical and physical chemical point of view (Holm et al., 2011; Chen et al., 2015). Particularly processes changing the nature of the carbon skeleton have been the topic of recent studies. In photodissociation regions (PDRs) in space, (large) PAHs (with more than 50 C-atoms) are considered starting points in the formation of other species, including fullerenes, carbon cages and smaller hydrocarbon chains (Pety et al., 2005; Berné and Tielens, 2012; Zhen et al., 2014b; West et al., 2012). **PAHs with functional side groups may also be** important. Inside molecular clouds, PAHs are expected to be trapped in low temperatures (~ 10 K) ice mantles (Guennoun et al., 2011b,a), consisting mainly of H_2O with traces of CH_3OH , CO_2 , CO , and NH_3 . Photolysis of these complex ice mixtures is known to functionalize PAHs with alcohol (-OH), ketone ($>C=O$), amino (- NH_2), methyl (- CH_3), methoxy (- OCH_3), cyano/isocyno (- CN , - NC), and carboxyl (- $COOH$) groups (Bernstein et al., 2002; Cook et al., 2015). When molecular cloud ices are exposed to the strong radiation field of a newly formed massive star in a PDR, ice molecules can be returned to the gas phase through various processes (Tielens, 2013). Photolysis of these newly formed PAHs with functionalized side-group additions, like methyl, methoxy, hydroxyl or carbonyl groups may play a comparable important role (Bernstein et al., 2002).

Quinones mainly dissociate through consecutive losses of carbonyl units (Beynon et al., 1959; Proctor et al., 1981; Pan et al., 2008). Their fragmentation mechanisms are well established for small species, e.g. substituted 1,4-naphthoquinone (Becher et al., 1966; Mari et al., 1966; Stensen and Jensen,

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