Radiation Physics and Chemistry 80 (2011) 38–43

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

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

EPR study of gamma irradiated 2,5-di-tert-butyl-hydroquinone single crystals

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ARTICLE INFO

Article history:
Received 22 April 2010
Accepted 27 August 2010

Keywords:
EPR
Spectroscopic splitting factor
g-factor
Isotropic hyperfine coupling constant *a*
DFT calculations
2,5-di-tert-butyl-hydroquinone (DTBHQ)

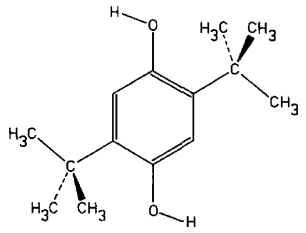
ABSTRACT

γ-irradiated single crystals of 2,5-di-tert-butyl-hydroquinone (DTBHQ) were investigated using the electron paramagnetic resonance (EPR) technique. The spectra of the crystals at different orientations in the magnetic field between temperatures of 120 and 450 K, were found to be temperature dependent.

Taking into consideration the chemical structure and the experimental spectra of the irradiated single crystals of DTBHQ, we assumed that one or more paramagnetic species were produced, each having an unpaired electron delocalized in the phenyl ring. Pursuant to this assumption, four possible radicals were modeled using the B3LYP/6−31+G(d) level of density-functional theory. EPR parameters were calculated for these modeled radicals using the B3LYP method and TZVP basis set. The calculated hyperfine-coupling constants were used as starting points for simulations. The experimental and simulated spectra for each of the three crystallographic axes were well matched for the modeled radical R4; we thus identified the hydroquinone anion radical as a paramagnetic species produced in DTBHQ. The experimental *g*-factor of the hydroquinone anion radical were found to be anisotropic with the average value $g_{iso}=2.0096$. The hyperfine coupling constants of the H_α proton was found anisotropic with the average value $(a^{\alpha}_{H7})_{iso}=6.3\ G$ and H_β proton was found isotropic with the average value $(a^{\beta}_{H8})=3.5\ G$.

1. Introduction

Free radicals can damage the cells and may play a role in heart disease, cancer and other diseases. Antioxidants are substances that may protect cells against the effects of free radicals. It is known that quinone derivatives especially hydroquinone and its certain derivatives are capable of inhibiting free-radical fragmentation reactions, which play an essential role in the damage of biologically important molecules (Cotele et al., 1991; Shadyro et al., 2002; Yamaguchi et al., 2006). 2,5-di-tert-butyl-hydroquinone (DTBHQ), an important derivative of hydroquinones, is used as an inhibitor, antioxidant and stabilizer.



It is useful as an antioxidant for rubber products, a stabilizer and an anti-skinning agent in paints. There are several investigations about antioxidant property of DTBHQ (Okubo et al., 1997; Kabbara and Stephenson, 1997; Tang et al., 2008), but the magnetic property of DTBHQ after irradiation of its single crystal has not been studied by EPR.

EPR is a magnetic resonance technique, which has been widely used in the identification of irradiation damage centers in many substances (Birey et al., 1997; Aras et al., 2006). To learn more properties of DTBHQ we have decided to investigate the magnetic properties of the irradiated sample by the EPR technique.

It is known that the EPR spectroscopy is one of the most powerful methods for studying the structure and determining the identity of molecules containing unpaired electrons. There are two EPR parameters (the **A** and **g** tensors) that contain valuable information about the geometry and electronic structure of the radical systems. The **A** value of a given nucleus in a radical is highly sensitive to its chemical environment. Hence, this can be used not only to determine the spin-density distribution of the radical, but also to deduce valuable information about the identity and structure of the radical. In contrast to **A**, the **g**-tensor quantity depends on the spin distribution in the whole radical. As a consequence, it can be significantly affected by intermolecular

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doi:10.1016/j.radphyschem.2010.08.017

interactions, thus providing valuable indications of the local environment of the radical (Ciofini et al., 2004). However, extraction of this information from experimental spectra is not always straightforward and, therefore quantum-chemical calculations are needed (Harriman, 1978; Turkkan et al., 2009; Sayin et al., 2010). The most accurate method of determining the

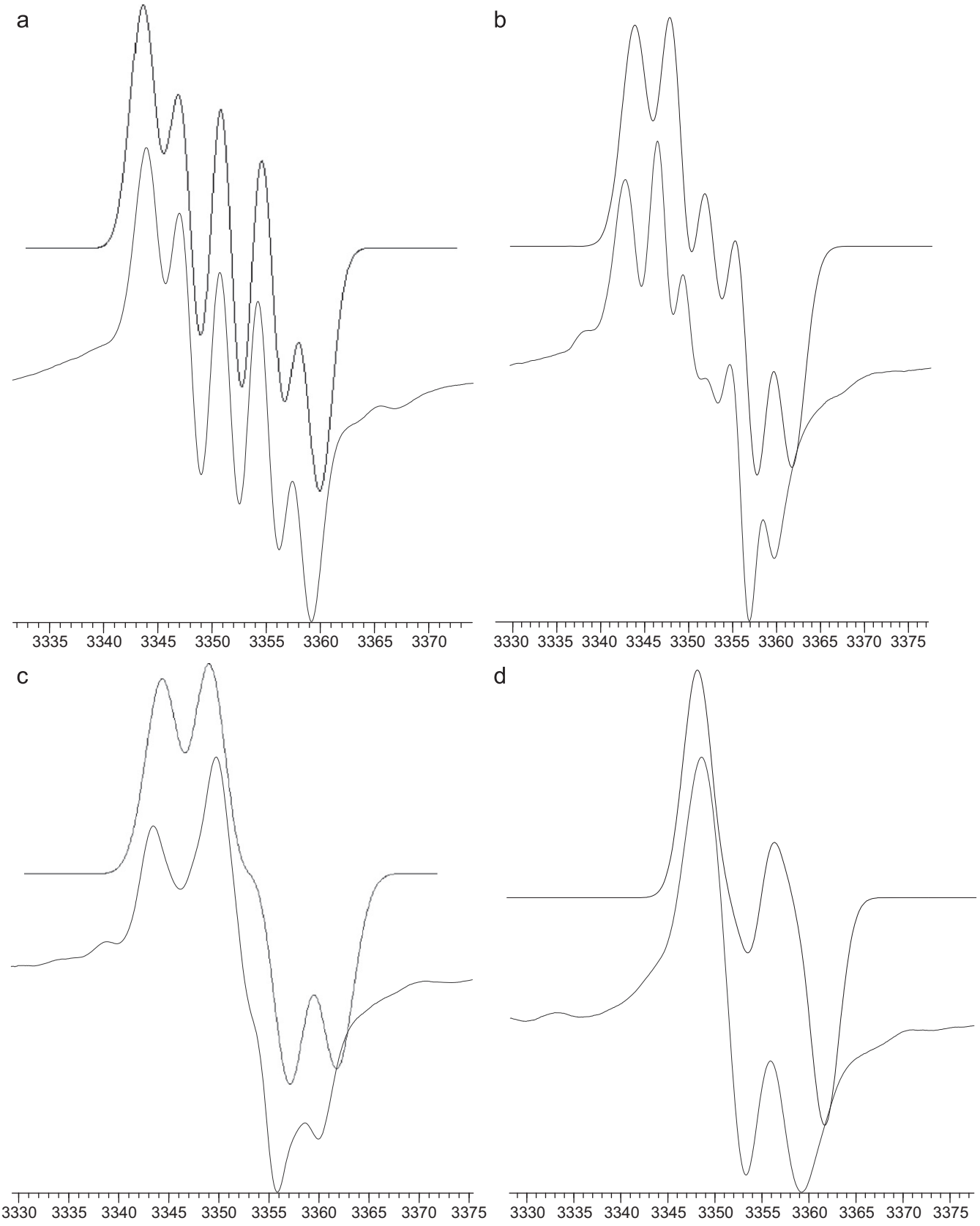

Fig. 1. Lower curve: EPR spectra of DTBHQ at 123 K when the magnetic field oriented (a) 10° (b) 30° (c) 60° (d) 110° to the *x*-axis upper curve: simulation of the relevant spectra.