ESR, ENDOR, and ESEEM Investigations on UV-Irradiated 2,4,6-Tri-tert-Butyl Phenol Crystals


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Abstract. Electron spin resonance (ESR), electron nuclear double resonance (ENDOR), and electron spin echo envelope modulation (ESEEM) measurements were carried out for UV-irradiated 2,4,6-tri-tert-butyl phenol in the polycrystalline state. The radical produced in the crystal was detected by ESR and identified to be the corresponding phenoxyl radical, which is well characterized in the chemical oxidations in solutions. ENDOR and ESEEM spectra were unambiguously analyzed in terms of the hyperfine coupling constants determined from well-resolved ESR in solutions. Radical pairs in the crystals were also ascertained, and together with the single-crystal study the analysis disclosed zero-field splitting parameters in the triplet states. ESEEM time decays gave relaxation times $T_1 = 5.94$ and $T_2 = 1.12$ µs at room temperature. These appropriate values permit an easy detection of the spin echoes, and therefore this radical matrix can be used as a useful standard for pulsed ESR investigations.

1 Introduction

It has long been appreciated that phenoxyl radicals are intermediates in many phenol oxidations, and, in particular, many stable radicals derived from 2,6-di-tert-butyl phenol derivatives have been ascertained in solutions by electron spin resonance (ESR) spectroscopy [1]. Oxidation reactions with chemical reagents such as potassium ferricyanide or lead dioxide yield almost quantitatively the corresponding radicals through abstraction of a hydrogen atom from a phenolic hydroxyl group. On the other hand, these phenoxyl radicals can be formed in detectable amounts by physical methods (irradiation, flash photolysis) [1]. The present study focuses on a freshly recrystallized 2,4,6-tri-tert-butyl phenol which has a tinge of slightly pale blue. Careful examinations with ESR spectroscopy indicated paramagnetic contamination, implying an oxidation of the phenol to a...
corresponding phenoxyl radical, probably through photochemical reactions. Thus, 2,4,6-tri-tert-butyl phenol was UV-irradiated so as to yield enough radicals to observe ESR and characterize the paramagnetic species. We carried out ESR, electron nuclear double resonance (ENDOR), and electron spin echo envelope modulation (ESEEM) measurements to elucidate the paramagnetism in detail. It was found that 2,4,6-tri-tert-butyl phenoxyl is dispersed in the corresponding diamagnetic phenol crystal and that this radical matrix works as a useful standard for continuous wave as well as pulsed ESR investigations.

2 Experimental

2,4,6-Tri-tert-butyl phenol was commercially available from Wako Chemicals Ltd. in Japan and used after recrystallization from ethanol several times (melting point 131°C). A little transparent single crystal with pale blue color was pulverized for polycrystalline measurements.

UV irradiation was performed in vacuo for 4–5 h with a high-pressure mercury lamp manufactured by Ushio Electric Inc. [2]. ESR and ENDOR measurements were carried out with JEOL 3FEX spectrometers. As for ENDOR measurements details were described elsewhere [3, 4]. Details of pulsed ESR studies on a JEOL PX1050 spectrometer were also given previously [5, 6]. For primary and stimulated spin echo measurements we employed \( t-\tau-2t \) and \( t-\tau-t-T-t \) (\( t = 30 \) ns) pulse sequences, respectively.

3 Results and Discussion

Radical production versus UV irradiation time is exhibited in Fig. 1, which indicates rapid production in the first stage and slower increase after one hour, approaching to a constant radical concentration. Spin counting of the irradiated sample after 2 h disclosed the radical concentration of 0.3%. This value is variable from 1 to 0.1%, depending on the irradiation conditions. Under ambient conditions no oxygen deterioration was detected in the solid state, unlike easy peroxide productions in solution.

ESR spectra of the UV-irradiated polycrystalline sample shown in Fig. 2 were composed of an intense but slightly asymmetric absorption and several weak lines on both sides. The main line (whose \( g \)-value and linewidth at the maximum slope are 2.0045 and 0.75 mT, respectively) comes from the isolated radicals produced by irradiation, which could be identified by ENDOR as well as ESEEM measurements. The asymmetry is probably due to the \( g \)-value anisotropy. With higher amplification (more than 100 times), several additional paired peaks could be observed (Fig. 2). These weak lines on both sides seem to be analyzed on the basis of radical pairs with \( S = 1 \). These absorptions will be discussed later. In order to obtain detailed hyperfine interactions for the central main species, ENDOR measurements were carried out, the spectrum being given in Fig. 3. There exist three paired lines centered at 14.20 MHz. The hyperfine coupling