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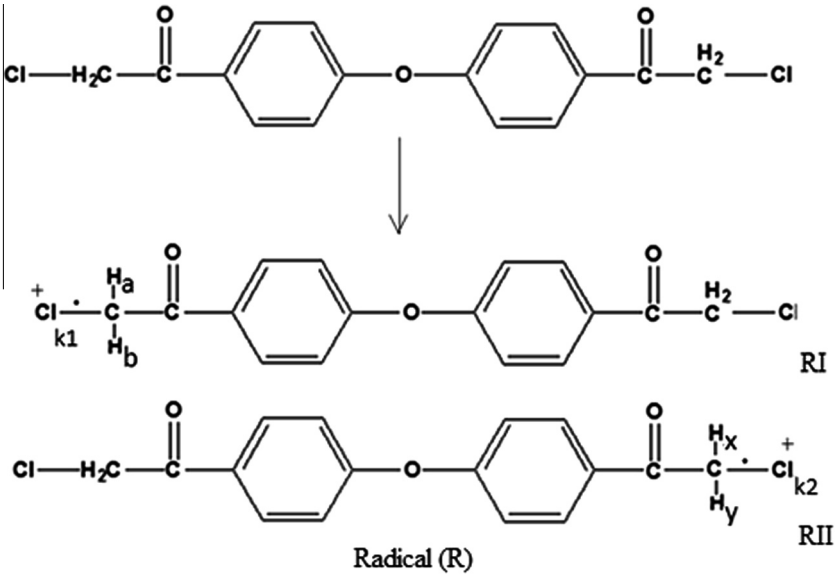
Determination of free radical on polycrystal of 4,4′-bis(chloroacetyl)diphenylether: An ESR study

Yusuf Ceylan [a], Ayhan Usta [b,*], Keziban Usta [b], Fatih Durmaz [c], Ahmet Coşkun [d]

[a] Department of Physics, Selcuk University, Konya, Turkey
[b] Faculty of Alanya Engineering, Akdeniz University, Antalya, Turkey
[c] Department of Chemistry, Selcuk University, Konya, Turkey
[d] Department of Chemistry Education, Necmettin Erbakan University, Konya, Turkey

GRAPHICAL ABSTRACT

The ESR spectra analysis indicated the formation of two identical radicals on irradiated 4,4′-bis(chloroacetyl)diphenylether polycrystal. It was determined that the produced radical structures on 4,4′-bis(chloroacetyl)diphenylether irradiated were stable.



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ABSTRACT

4,4′-Bis(chloroacetyl)diphenylether was synthesized and its polycrystal form was produced. This polycrystal sample was irradiated by gamma rays (^{60}Co) for 72 h. The ESR method was used to observe formation of free radical on the sample. ESR signal was not recorded from the non-irradiated sample, but the irradiated polycrystal sample exhibited complex ESR spectra. The measurements were carried out in the temperature range of 120–450 K. It was observed that the shape of the spectrum was dependent on the temperature. Two identical radicals were determined on the irradiated sample. Respectively, the spin density, hyperfine, and g values were found to be $\rho_{Ha} = 0.53$, $\rho_{Hb} = 0.23$, $a_{Cl} = 1.263$ mT, $a_{Ha} = 1.486$ mT, $a_{Hb} = 0.637$ mT, and $g_1 = 2.0115$ for the Radical I; $\rho_{Hx} = 0.22$, $\rho_{Hy} = 0.14$, $a_{Cl} = 0.905$ mT, $a_{Hx} = 0.615$ mT, $a_{Hy} = 0.391$ mT, and $g_2 = 2.0383$ for the Radical II.

* Corresponding author. Tel.: +90 242 518 2266; fax: +90 242 518 2277.
E-mail addresses: yceylan@selcuk.edu.tr (Y. Ceylan), austa@akdeniz.edu.tr (A. Usta), kusta@akdeniz.edu.tr (K. Usta), fdurmaz@selcuk.edu.tr (F. Durmaz), acoskun42@gmail.com (A. Coşkun).

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1. Introduction

Diphenyl ether derivatives are important compounds. They have been widely used in textiles and computer materials [1]. Polybrominated diphenyl ethers (PBDE) are added as flame retardants to many kinds of polymers [2], and PBDE residues have been found in human blood plasma [3]. While early reports indicate low toxicity for PBDEs [4], some later studies suggest that they are more harmful than previously believed [5]. It is known that irradiation has a significant role on chemical materials as well as foods [6]. For example, ionizing radiation is able to kill the pathogens in contaminated foods; moreover, irradiation can also cause modification of physical properties [7]. However, irradiation can cause scission of bonds [8,9] and toxic structure. The electron spin resonance (ESR) technique has frequently been used for the identification of irradiation damage centers in organic and inorganic substances [10–13]. In the present study, 4,4′-bis(chloroacetyl)diphenylether polycrystal sample exposed to gamma rays was investigated in the temperature range of 120 K and 450 K through ESR method.

2. Experiment

2.1. Synthesis of 4,4′-bis(chloroacetyl)diphenylether

4,4′-Bis(chloroacetyl)diphenylether was prepared according to the literature methods [14,15] . Diphenylether (2.8 mL, 17.3 mmol) was dissolved in CH_2Cl_2 (5 mL) and the solution was added dropwise to a suspension of anhydrous $AlCl_3$ (5.8 g, 43.4 mmol) and chloroacetyl chloride (3.1 mL, 38 mmol) in CH_2Cl_2 (20 mL) along with cooling. The mixture was stirred in ambient temperature until the evolution of HCl ceased (about 12 h). After the removal of the solvent by rotary evaporator, the residue was recrystallized from EtOH. (4.02 g 70%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.90 (m,8H, Ar-H, 4.64 (s, 4H, $-CH_2-$). Anal. Calcd. for $C_{16}H_{12}Cl_2O_3$: C, 59.46; H, 3.74. Found: C, 59.24; H, 3.69. m.p: 108 °C [Lit:

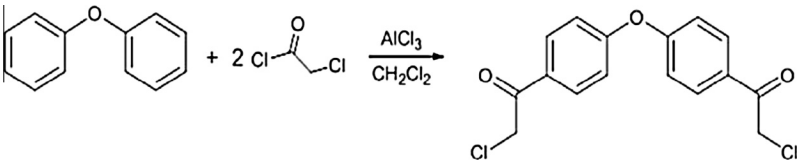


Fig. 1. The synthesis of the *4,4′-bis(chloroacetyl)diphenylether*.

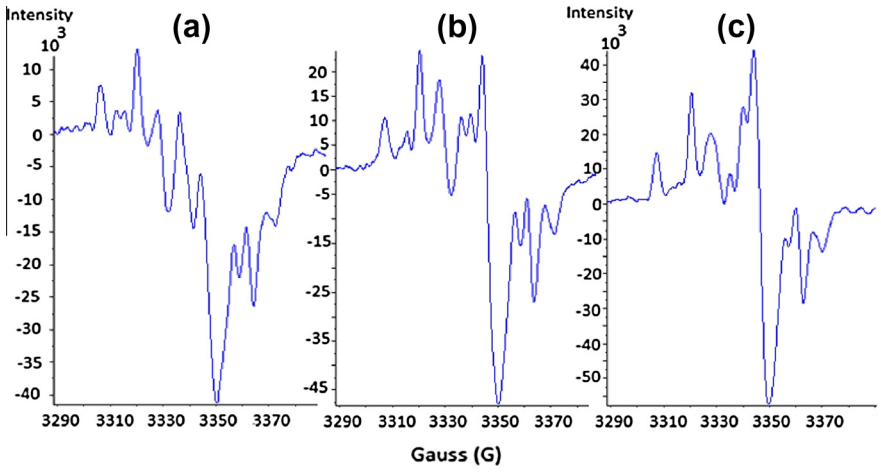


Fig. 2. Temperature dependence of the ESR absorption signal at 150 K (a), 250 K (b) and 400 K (c).

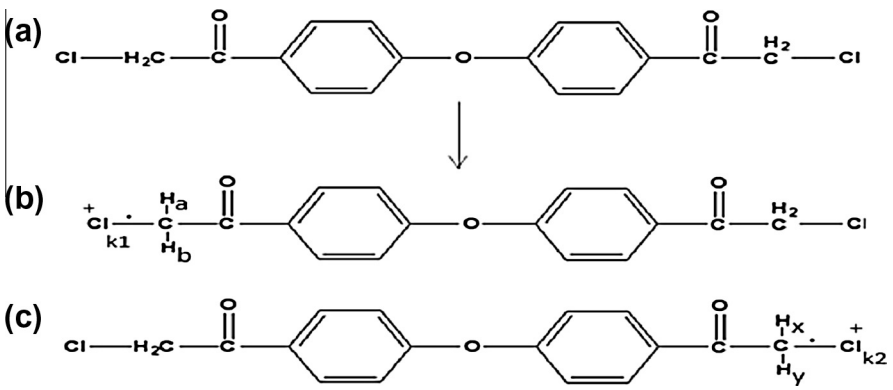
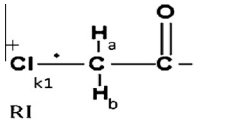
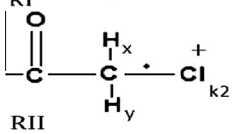


Fig. 3. Molecular structure (a), the radical structures (b and c) of the 4,4′-bis(chloroacetyl)diphenylether polycrystal sample.

Table 1
The ESR parameters of free radicals produced by γ-irradiation on 4,4′-bis(chloroacetyl)diphenylether. The error for all calculated *g*-values is estimated as ±0.0005 and for hyperfine splittings is ±0.05 mT.

Radical	Hyperfine splittings	Spin density	*g*-Values
 RI	$a_{Cl_{k1}} = 1.263$ mT $a_{Ha} = 1.486$ mT $a_{Hb} = 0.637$ mT	 0.53 0.23	 2.0115
 RII	$a_{Cl_{k2}} = 0.905$ mT $a_{Hx} = 0.615$ mT $a_{Hy} = 0.391$ mT	 0.22 0.14	 2.0383

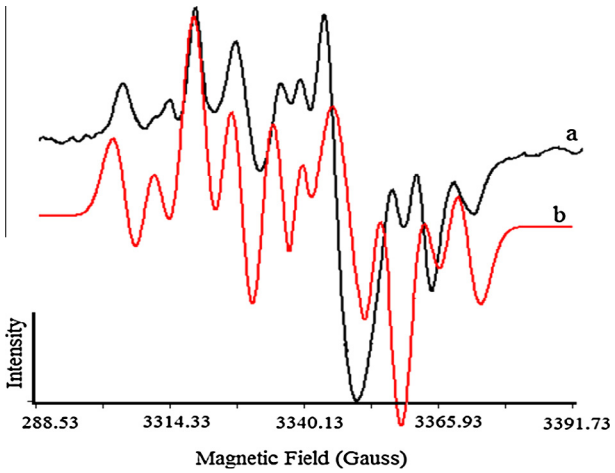


Fig. 4. The ESR spectrum of a γ-irradiated 4,4′-bis(chloroacetyl)diphenylether (a) and the simulation of the spectrum for RI + RII (b).

108–109.5]. The synthesis of the *4,4′-bis(chloroacetyl)diphenylether* is shown in Fig. 1.

2.2. Crystallization

4,4′-Bis(chloroacetyl)diphenylether was prepared according to the literature methods [14] from chloroacetylchloride and diphenylether in the presence of $AlCl_3$ as catalyst in a Friedel–Crafts reaction.

2.3. ESR measurement

In the study, the sample used was polycrystal and in solid form and the grain size of crystals was less than 0.05 mm. The polycrystal sample was irradiated for 72 h by ^{60}Co γ-ray source with dose speed of 0.981 kGy/h. ESR spectra were recorded using Bruker EMX 081 spectrometer (X-Band, Germany). The spectrometer was set as follows: microwave power was 5 mW, modulation frequency of magnetic field was 100 kHz, and modulation amplitude was 0.2 mT (Tesla), and microwave–frequency was 9.390 GHz. The high and low temperature measurements were performed between 120 K and 450 K using temperature control unit of the spectrometer.

3. Results and discussion

ESR signals were not observed on non-irradiated 4,4′-bis(chloroacetyl)diphenylether. However, the ESR spectra were recorded from the polycrystalline sample irradiated for 72 h. The measurements were performed in the temperature range of 120–450 K. It was observed that the shapes and intensities of the lines in the spectra changed along with temperature (Fig. 2). The obtained results may clarify that at lower temperatures free electrons are localized on the chlorine atom, but as the temperature increases, the free electron is delocalized between the chlorine and hydrogen atoms.

From the analysis of the spectra, it was understood that the distance between the lines in the spectra were different. We inferred from this result that two types of radicals were formed under gamma-rays. After the conduct of an in-depth analysis on the molecular structure and the spectra recorded, it was understood that both of these radical structures were identical, but the ESR parameters of the radicals were different and unpaired electron was produced by removing one of the paired electrons on chlorine atoms. Owing to the chlorine atom, the spectrum was split to 1:1:1:1 intensity ratios; then each line was split to 1:1 intensity ratio due to each hydrogen atom labeled as a and b which are magnetically non-equivalent. The interaction of the sample with gamma rays was attributed as shown in Fig. 3 and the radicals were labeled RI and RII (Fig. 3b and c).

The hyperfine coupling values, *g*-constants and spin densities of the radicals were obtained from experimental spectra as shown in Table 1.

Electron spin density (ρ) of the proton can be calculated by means of Mc Connell equality ($a = Q\rho$). Here Q is the resonance multiplier. For the hydrogen atom, Q_H is given 2.8 mT [9]. Table 1 indicates that unpaired electron spends a large portion of its time on hydrogen atom. Calculated hyperfine couplings and *g*-values were verified by computer simulation. There is a perfect match between the experimental spectra and computer simulation as shown in Fig. 4.

The measurements were performed at regular intervals in three days. From the obtained results, it was understood that produced radical structures on 4,4′-bis(chloroacetyl)diphenylether were stable.

4. Conclusion

The investigation showed that non-radiated polycrystalline sample did not have a radical structure. The ESR signals were recorded from the sample irradiated for 72 h. The ESR spectra analysis indicated the formation of two identical radicals on irradiated 4,4′-bis(chloroacetyl)diphenylether polycrystal sample. From the analysis of recorded spectra, it was determined that the produced radical structures on 4,4′-bis(chloroacetyl)diphenylether were stable.

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