

EPR Study of the Thermal Decomposition of Transannular Peroxide of Anthracene

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Abstract

Thermal decomposition of transannular peroxide of anthracene (POA) (or 9,10-epidioxido anthracene) was studied by means of electron paramagnetic resonance spectroscopy (EPR) in the solid as well as in the liquid phases. Decomposition process proceeds via cleavage of the O-O bridge of the POA molecule, generating thus an alcoxy intermediate radical. Its concentration increases to a certain equilibrium stage during the time scale of the experiment. EPR spectra in the solid state were of the singlet type at the temperatures over 350 K, a doublet like anisotropic spectra were measured at the room temperature, both having g -value 2.0033. EPR spectrum from POA decomposed in benzene indicates four protons with higher ($2a_H = 0.305$ mT, $2a_H = 0.335$ mT) and four protons with a lower ($2a_H = 0.075$ mT, $2a_H = 0.105$ mT) splitting constants, corresponding well the radical expected after cleavage of O-O bridge.

Keywords: Endoperoxide, Anthracene, Free Radicals, EPR, Decomposition, Kinetics

1. Introduction

UV light irradiated anthracene and its derivatives in degassed solutions give anthracene dimers, while in the presence of oxygen they form endoperoxides [1,2]. As found by quantum chemical molecular orbital calculations based on Woodward-Hoffman orbital symmetry conservation principle application [3], endoperoxides of anthracene production is catalysed by transition metals atoms. These thermally and photochemically reactive substances (depending on the reaction conditions) are decomposed to the original hydrocarbon and simultaneously liberate singlet oxygen (1O_2), or decompose by the disruption of the O-O bonds, thus producing highly reactive biradical, or finally by the transformation into the other types of peroxides [4]. For instance, for anthracene-9,10-endoperoxide (POA) it has been found, that its photochemical excitation to S_n , with $n \geq 2$ leads to cycloreversion, producing anthracene and 1O_2 , whereas excitation to the S_1 state would initially cause homolytic O-O cleavage, eventually resulting in a diepoxide rearrangement product [5,6].

Decomposition via disrupting of the O-O bridge can be used for an effective crosslinking of some industrially

important polymers, producing thus highly crosslinked matrices, e.g. for the optical information storage [7]. In contrary to the latter mentioned polymer matrix crosslinking reactions, depending on the reaction conditions, a vigorous degradation of polysaccharide hyaluronic acid by singlet oxygen liberated from POA was reported earlier [8]. The possibility of endoperoxides to release these reactive species by unimolecular decomposition makes them interesting candidates for in vivo site-specific oxidative targeting with singlet oxygen at the present time [6,9]. The complex oxygen photosensitization in the presence of water soluble anthracene-1-sulphonate was studied by means of EPR spin trapping method [10]. It was found, that the anthracene-1-sulphonate in the presence of oxygen is converted to quinone and oxygen is activated to superoxide radical intermediate. Consecutively, the latter superoxide radicals are transformed into the highly reactive hydroxyl radicals.

In the paper presented thermal decomposition of transannular peroxide of anthracene (or anthracene 9,10-endoperoxide, or 9,10-epidioxido-anthracene) is studied by means of electron paramagnetic resonance spectroscopy (EPR) both in the solid as well as in the liquid phase.

2. Experimental

2.1. Materials

Transannular peroxide of anthracene was synthesized using photosensitized reaction with methylene blue as a photo sensitizer in chloroform by the method described earlier by Foot *et al.* [2,11]. Final product was then purified using column chromatography (Florosil, Fluka, Switzerland) and then several times re-crystallized in vacuum. All chemicals used during synthesis were of analytical grade purity. Final colourless crystals were identified and characterized by IR spectroscopy [11] characteristic absorption bands at 1170, 950, 880, 846, and 745 cm^{-1} wavenumbers as shown in **Figure 1**, UV VIS spectroscopy [12] and GC-MS [13].

2.2. Methods

Infra red spectra (IR) were recorded on computer controlled Perkin Elmer 983 spectrometer (USA).

Electron paramagnetic resonance spectra were measured at room temperature on Bruker 200E SRC spectrometer controlled by Aspect 2000 computer (Bruker, Germany). All EPR spectra were simulated using standard simulation software EPRSRC (Bruker, Germany).

3. Results and Discussion

In **Figure 2** are shown EPR spectra of POA thermal decomposition product as observed in the solid sample at

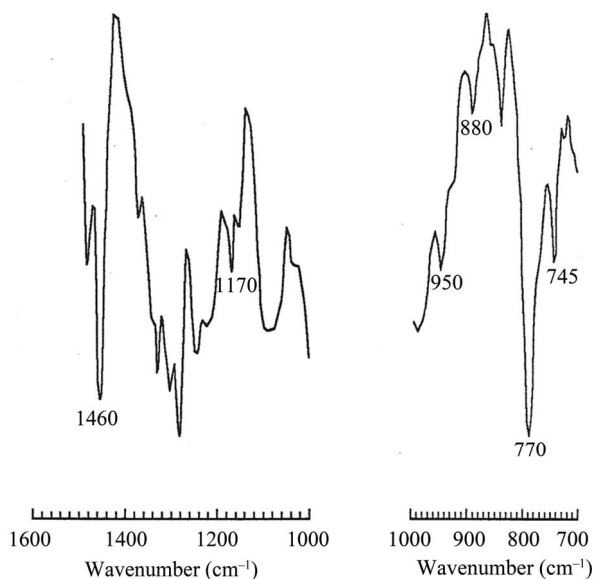


Figure 1. IR spectrum with the labelled characteristic absorption bands of POA measured in the form of thin film prepared by evaporation of solvent (CDCl_3) on KBr lens.

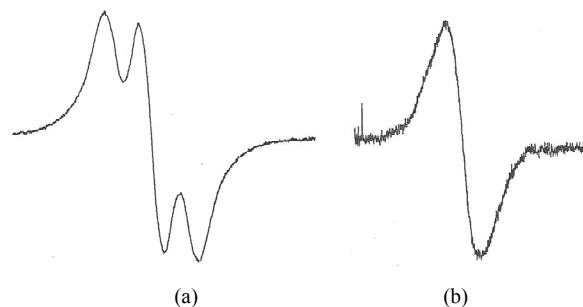


Figure 2. EPR spectra of POA measured in the solid sample at temperature: (a) 300 K; (b) 350 K ($SW = 5.0$ mT, $g = 2.0033$).

two different temperatures. Doublet anisotropic EPR spectrum measured at 300 K was vanishing with the increasing temperature, while at about 350 K the singlet spectrum was observed. Probably, the hyperfine anisotropic structure of the EPR spectrum at lower temperature was possible to follow due to the polycrystalline character of the studied sample. As the temperature was increased to the temperature close to the melting point (values given in the literature are ranging from 120°C up to 160°C (Ref. [4]) the slightly anisotropic character disappears and only purely isotropic singlet EPR spectrum was observed. For both, the doublet as well as the singlet spectrum the same g -factor was observed ($g = 2.00330$), suggesting the same kind of the intermediate radical. The time dependence of the intensity of the EPR line measured at 273 K is shown in **Figure 3**. Here, the intensity of the signal is increasing with the time suggesting increasing radical concentration in the system. After several minutes, it is reaching its time independent plateau, suggesting probably equilibrium radical concentration. The same dependencies were observed at 393 K, 413 K as well as at 433 K. At the temperature of 433 K, the

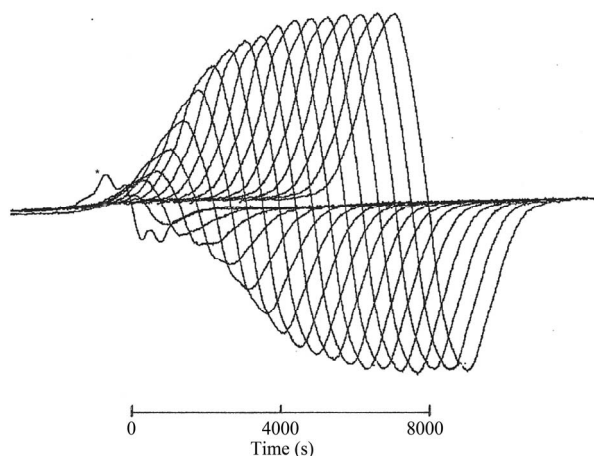


Figure 3. Time dependence of EPR spectra evolution measured at 373 K (*spectrum measured at room temperature).

intensity of the EPR spectrum after reaching its maximum decreases. Most probably, the POA is starting to decompose at this temperature. This phenomenon is more evident from **Figure 4**, where the kinetic curves of the time dependencies of the EPR line intensities measured at the different temperatures are shown. The initial slope is decreasing at the lower temperature. This indicates that the rate constant of the radical generation is decreasing.

Formal first order kinetic rate constants of these processes are given in the **Table 1**. It is evident, that with the increasing temperature the production of the radical intermediates is more effective.

Because of the fact, that the singlet EPR spectra cannot be unambiguously assigned to a defined structure, one can expect more exact structural information about the radical surrounding from the hyperfine splitting of the EPR spectra which can be observed in the solution. For this reason, we have studied the thermal decomposition of POA also in the liquid phase.

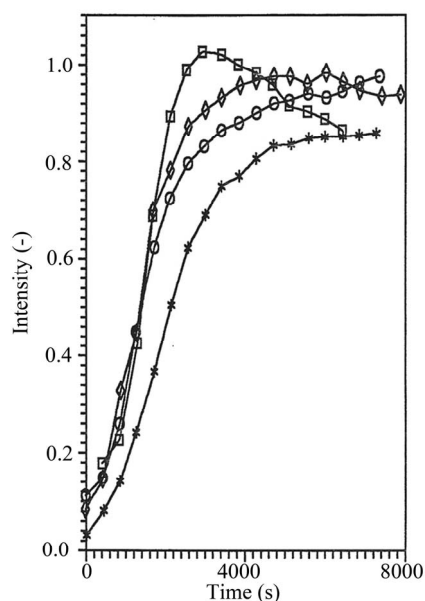


Figure 4. Time dependencies of the radical concentrations observed during thermal decomposition of POA at: star—373 K; Empty circle—393 K; Empty diamond—413 K; Empty square—433 K.

Table 1. Obtained values of the first order kinetic mechanism rate constants of POA thermal decomposition as calculated for data shown in **Figure 4**.

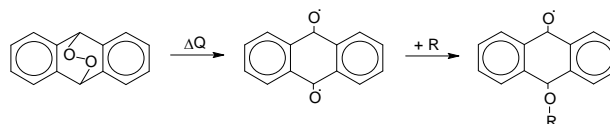
Temperature (K)	$10^4 \times k_1$ (1/s)	Corr. Coeff.
373	3.32	0.984
393	5.30	0.987
413	6.32	0.981
433	6.85	0.944

Figure 5 shows experimental and simulated spectra of POA in benzene as observed at 300 K. It was simulated with four higher ($2a_H = 0.305$ mT, $2a_H = 0.335$ mT) and four lower ($2a_H = 0.075$ mT, $2a_H = 0.105$ mT) splitting constants. This corresponds well to the two groups (every one with approximately four equivalent protons in xx and yy positions) own to POA structure.

To obtain a better fit between the experimental and simulated EPR spectrum, also a contribution singlet spectrum depicted in **Figure 2(b)** had to be considered by the simulation. Similar spectra were observed also at higher temperatures in different solvents (e.g. toluene, xylene, chloroform).

4. Conclusions

The analysis of EPR spectra shown in **Figure 5** monitored during the thermal decomposition of POA suggests formation of the following radicals:



where R is a radical capable to react with oxygen centred radical from anthracene. R^{*} may originate from the solvent molecules or from some another external sources. The scheme is in accord with earlier published results by Cowell and Pitts Jr. [14] assuming endoperoxide formation with consecutive radical reactions. Our theoretical investigations [3] implied the role of transition metal by the formation of anthracene endoperoxide. Lazar *et al.* [7] experimentally confirmed formation of alkoxy radicals during thermal POA decomposition, and, furthermore, analogous EPR spectra were found investigating similar systems [15].

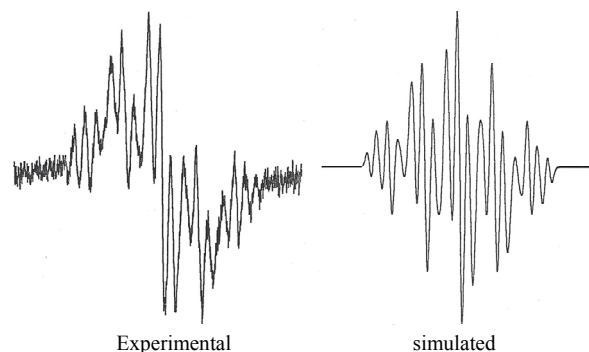


Figure 5. Experimental and simulated EPR spectra of POA dissolved in benzene during thermal treatment at 300 K, $g = 2.0034$, simulated as $2a_H = 0.075$ mT, $2a_H = 0.105$ mT, $2a_H = 0.305$ mT, $2a_H = 0.335$ mT, $pp = 0.045$ mT with the g -factor of 2.0034, $SW = 2.5$ mT. (a_H and pp are splitting constant and peak-to-peak width expressed in mT).

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