

Electron paramagnetic resonance study of radiation-induced paramagnetic centers in succinic anhydride single crystal



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ABSTRACT

Succinic anhydride single crystals were exposed to ⁶⁰Co- γ irradiation at room temperature. The irradiated single crystals were investigated at 125 K by Electron Paramagnetic Resonance (EPR) Spectroscopy. The investigation of EPR spectra of irradiated single crystals of succinic anhydride showed the presence of two succinic anhydride anion radicals. The anion radicals observed in γ -irradiated succinic anhydride single crystal were created by the scission of the carbon-oxygen double bond. The structure of EPR spectra demonstrated that the hyperfine splittings arise from the same radical species. The reduction of succinic anhydride was identified which is formed by the addition of an electron to oxygen of the C–O bond. The *g* values, the hyperfine structure constants and direction cosines of the radiation damage centers observed in succinic anhydride single crystal were obtained.

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1. Introduction

Radicals can be formed in three types of processes: irradiation (photolysis, radiolysis), thermolysis (thermal homolysis), redox processes (oxidation-reduction reactions) [1,2].

In irradiative processes, the energy necessary to form radicals can be supplied by any of the forms of electromagnetic radiation (ultraviolet or visible light, x-rays, etc.) or by corpuscular radiation (high-energy electrons; α , β , γ particles; neutrons; protons; etc.). To processes involving the absorption of light, a subdivision of radiation chemistry called photochemistry [1].

There are three main categories of ionizing or high-energy radiation devices developed and used in practice [3–5]: Charged particle accelerators (X-ray generators; medium energy electron accelerators; Van der Graaff accelerator); radioisotope sources (⁶⁰Co γ -ray source; ¹³⁷Cs γ -ray source; spent fuel elements); nuclear reactor (mixed radiation of gamma quanta and neutrons). Of these three, the ⁶⁰Co γ -ray source is found to be the most convenient and easily-controlled [6,7].

Interaction of matter with “ionizing radiation”, i.e. high-energy electromagnetic radiation (X- or γ -rays) or α - or β -particles, can

promote chemical change which commonly involves free radicals. The ionizing radiation can produce the reactive radicals [8].

It is well known that radiation breaks bonds between atoms in molecules. If the bonds are broken homolytically, free radicals result. If the bonds are broken heterolytically (diamagnetic), ionic fragments result [9].

When an organic material is irradiated, the bonds between atoms can be broken. The minimum energy required to break these bonds is determined by the strength of the bond itself. Most bond strengths correspond to wavelengths in the ultra-violet region and the energy required can often be determined by varying the wavelength of the incident radiation. X- or γ -ray irradiation corresponds to much greater energies, and a larger number of bonds can therefore be broken. This usually gives a high concentration of free radicals, but as a greater variety of damage mechanisms are possible and spectra may even overlap, identification is less certain [10,11].

Irradiation of inorganic materials (often in the form of single crystals) produces damage centres trapped within the crystal lattice, and may cause the breaking of chemical bonds, or the formation of free atoms, molecules or radicals, which can be stabilized within the crystal.

Often spectra cannot be observed, owing to the fast recombination of these radicals, as the concentration of radicals formed is purely a balance between the rate of formation and the rate of

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recombination. Sometimes even the relaxation time is too short. However, these difficulties can generally be overcome by stabilizing the radicals at low temperatures [10].

The rate of recombination will depend to a great extent on the viscosity of the sample, although for X- or γ -ray irradiation there is always sufficient energy imparted to the broken bonds for them to move away with some speed. They therefore become trapped in the solid at a sufficient distance apart to prevent recombination, and so radicals can be formed and trapped no matter how viscous or rigid a solid may be. If ultra-violet irradiation is used, the broken bonds have less energy after the bond fission, and if the sample is too viscous, the radicals may not be able to move apart and will recombine immediately. The solid must also be rigid enough to hold the radicals apart after their initial formation, so clearly some compromise must be reached. One way of doing this is to dissolve the samples to be irradiated in various hydrocarbons, and then to freeze the solution at liquid nitrogen temperatures to form rigid glasses [12]. The viscosity of the medium can then be altered by either varying the constitution of the hydrocarbon mixture or by altering the temperature [10].

Another very important action induced by irradiation of solids containing hydrogen, is the abstraction of the hydrogen atoms. As the excitation energy of the irradiating source is quite often considerably more than the binding energy, a small fraction of the hydrogen atoms abstracted may possess very high energy and will display specific chemical properties. Hydrogen atom reactions and a high level of irradiation in, say, solid hydrocarbons can only be judged by their secondary reaction products, and EPR is an ideal tool for the analysis of these complex radicals. For example, in frozen aqueous solutions of H_2SO_4 , H_3PO_4 or HClO_4 , H atoms are quite stable at liquid nitrogen temperatures (77 K) and this provides excellent opportunities for further study.

Secondary reaction radicals can also be formed in solids irradiated by ultra-violet or high velocity electrons, and evidence has been presented showing the existence of these secondary radicals in irradiated polymers [10].

Ingram and his co-workers [12] were the first to obtain evidence of secondary radical reactions in a frozen hydrocarbon solvent at liquid nitrogen temperatures. Primary hydroxyl radicals were produced by photolysis of hydrogen peroxide and a secondary reaction produced isopropanol radicals. Radicals may even be formed in water by irradiation with high voltage X-rays. One other typical example of hydrogen abstraction is the irradiation of frozen cyclohexanol.

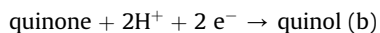
Free radicals formed by high energy radiation in solids can then be identified by analysis of their EPR spectra. The radical formation may be due to bond breakage, to crystal imperfections, or to secondary radicals produced by abstraction of hydrogen atoms [10].

The usual practice in using EPR as a tool in the study of the radiation chemistry of the chemical compounds is to irradiate the compounds and observe the EPR spectrum at 77 K, at which temperature the free radicals can be considered immobile, i.e. trapped. If the sample is then allowed to warm up to room temperature, and the reactions and decay of the free radicals followed, information is given not only on the radiation chemistry, but also on the solid state reactions taking place [10].

Succinate:quinone reductase (SQR) of complex II occupies a unique central point in the mitochondrial respiratory system as a major source of electrons driving reactive oxygen species (ROS) production. It is an ideal pharmaceutical target for modulating ROS levels in normal cells to prevent oxidative stress-induced damage or alternatively, increase ROS in cancer cells, inducing cell death [13].

As for the superfamily of succinate:quinone oxidoreductases (SQOR, EC 1.3.5.1) as a whole [14,15], the di-heme family of

respiratory complex II enzymes couple the two-electron oxidation of succinate to fumarate (reaction a) to the two-electron reduction of quinone to quinol (reaction b):



The molecular structures of succinate, fumarate, quinone and quinol are shown in Figs. 1–4, respectively.

They can also catalyse the opposite reaction, the coupling of

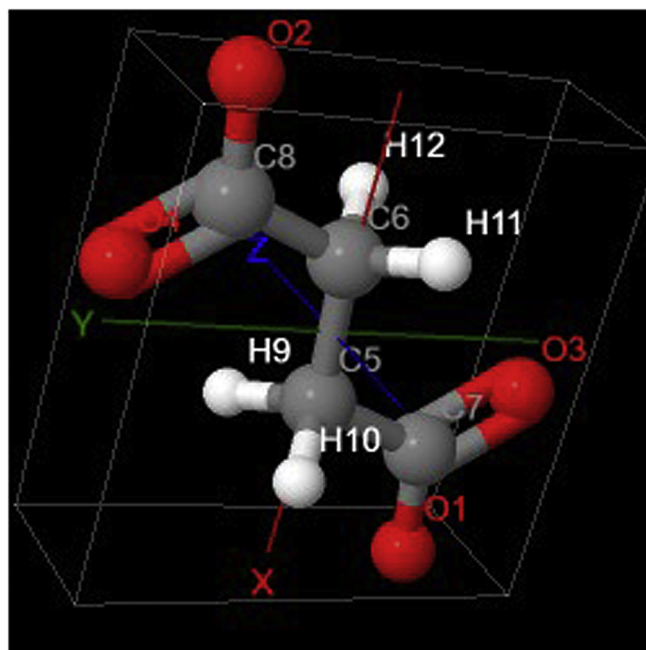


Fig. 1. Molecular structure of succinate ($\text{C}_4\text{H}_4\text{O}_4$).

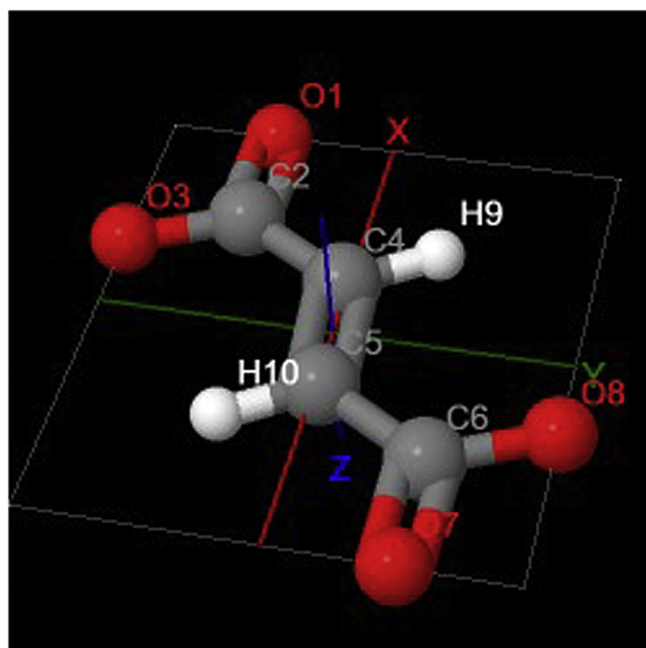


Fig. 2. Molecular structure of fumarate ($\text{C}_4\text{H}_2\text{O}_4^{2-}$).

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