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On the absence of CO_2^- in irradiated succinic acid*

P. Premović, O. Gal, and B. Radak

Boris Kidrič Institute of Nuclear Sciences, Vinča - Belgrade, Yugoslavia

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The numerous electron spin resonance studies on irradiated succinic acid have shown that at least three radical fragments exist at ambient temperature[1-8]: (a) $HOOCCH_2\dot{C}HCOOH$, (b) $CH_3\dot{C}HCOOH$ (in small amounts), and (c) $\dot{C}O_2^-$, the carbon dioxide anion radical. However, the last species which gives rise to a single line in ESR spectrum was recently put into doubt.

It was believed that this "singlet" is produced from decay of a negative ion primary[3] and that its *g* tensor is sufficiently similar to that of $\dot{C}O_2^-$ ion-radical for it to be identified as such.[8] However, McCalley and Kwiram revised this last conclusion recently.[9] Using the singlet data reported by Schwartz *et al.*,[8] they have calculated the directions of the principal axes relative to the carboxylic framework of the crystal structure of succinic acid. From this revision it came out that the *g*-tensor orientation of the singlet in succinic acid is identical within 2° to that of the acyl radical in malonic acid.[10] Thus, they concluded that the singlet in succinic acid has the structure $HOOCCH_2CH_2\dot{C}{=}O$. Muto *et al.* in their more recent comprehensive ESR study of irradiated succinic acid[11] gave a mechanism of formation of this radical.

In some of our earlier ESR measurements[12] we obtained a similar *g* tensor for the singlet in irradiated succinic acid as reported in Ref. 8 and, in addition, found that the orientation of the principal axes of the *g* tensor also differed from those for CO_2^-. (At that time we considered our results as erroneous and never published them.[12]) This time we would like to present further evidence, based on the ultraviolet (uv) and infrared (ir) spectra, that the singlet in succinic acid does not belong to the $\dot{C}O_2^-$ anion radical.

Single crystals of about 1×2×2 mm were grown from saturated aqueous solutions by slow evaporation. The crystals were irradiated at room temperature by ^{60}Co rays to doses ranging from 1 to 10 Mrad. uv spectra were obtained at ambient temperature with a Beckmann DK-1A spectrophotometer. An unirradiated crystal was placed in the reference beam of this double beam instrument. The measurements have shown that an irradiated succinic acid single crystal has a weak band at about 300 nm and a stronger one at around 240 nm. Similar absorption bands were also recorded in irradiated samples of malonic acid. For comparison, the uv spectra of an irradiated sodium formate single crystal were recorded under the same conditions of irradiation and measurement. The data we obtained are in agreement with the uv spectra of the $\dot{C}O_2^-$ ion-radical in sodium formate which have been reported by Chantry and Whiffen[13]; we observed a weak band at about 340 nm and a stronger one at 275 nm. A third band of slightly

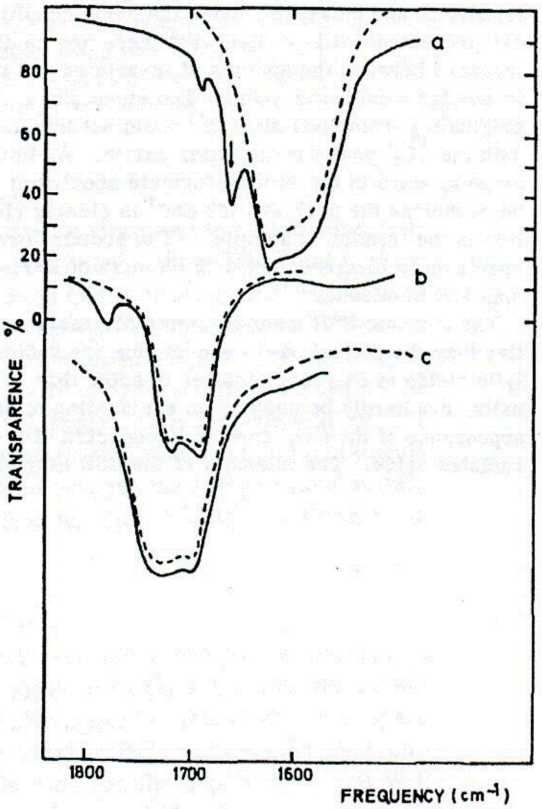

FIG. 1. ir absorption spectra of γ-irradiated (full lines) and unirradiated (dotted lines) substances in KBr matrix, recorded at room temperature: (a) sodium formate, (b) succinic acid, and (c) malonic acid. Curves displayed vertically for clarity. The arrow indicates the CO_2^- radical position.

greater intensity was found at 245 nm. The differences in the correlated spectra were evident.

In addition, the bright pink color, recently reported in irradiated malonic acid,[10] is also observed in irradiated succinic acid monocrystals. McCalley and Kwiram[9] associated this color with the $RCH_2-\dot{C}=O$ radical and compared it with the red coloration of acetyl radicals in hydrocarbon glasses. They attributed the absorption to the $\sigma \rightarrow \pi^*$ electronic transition which is also responsible for the low g-tensor value when the magnetic field is parallel to the C–O bond.

The ir measurements were made with a double beam Zeiss Model UR-10 spectrophotometer using the KBr disk technique and the procedure given by Hartman and Hisatsune.[14]

The typical spectrum of irradiated succinic acid is shown in Fig. 1. For comparison, the spectra of sodium formate as well as that of malonic acid irradiated and measured under the same conditions are presented. It is evident that there are no differences between the spectra of irradiated and unirradiated samples of acids. The steep slope originating from C=O stretch[15] could not interfere with the $\dot{C}O_2^-$ peak[14] if the latter exists. A similar slope appears in the sodium formate spectrum; nevertheless the peak at 1663 cm^{-1} is clearly visible in the irradiated sample. (The sodium formate spectrum is in agreement with the data of Hartman and Hisatsune.[14])

The fact that ESR measurements are more sensitive than the optical ones, and/or that the radiolytic yields of $\dot{C}O_2^-$ are smaller in acids than in salts, can hardly be used as an explanation of nonappearance of the $\dot{C}O_2^-$ band in the spectra of irradiated acids. The intensity of the ESR singlet in succinic acid indicates that the concentration of radicals in question is of the same order of magnitude as for the molecular CO_2 in the salts. Consequently, the $\dot{C}O_2^-$ band in the acids should be detectable, if present.

We believe, therefore, that the data presented here contributes to the idea that the $\dot{C}O_2^-$ radicals in irradiated succinic acid do not exist and that the ESR singlet might well be attributed to a radical of the $RCH_2\dot{C}=O$ type.

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