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ESR INVESTIGATION OF RADICAL REACTIONS IN γ-IRRADIATED FROZEN AQUEOUS SOLUTIONS OF FORMIC ACID AND FORMATE

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In studies of the reduction of CO_2 in aqueous solutions under the influence of gamma rays the formation of the CO_2^- radical ion and the COOH (or HCOO) radical have been proposed[1,2,3]. CO_2^- was observed in pulse radiolysis experiments[4]. CO_2^- and COOH have been shown to be important intermediates in the radiation induced carboxylation of organic compounds in aqueous solutions[5,6,7]. The following reaction mechanism has been suggested to explain the high yield of oxalic acid ($G = 9.1$ at p_H 10.8)[6,7] formed in the carboxylation of formic acid:

$$(1)\quad CO_2 + e^-_{aq} \longrightarrow CO_2^- + n\,H_2O$$

$$(2)\quad CO_2 + H \longrightarrow COOH \text{ or: } HCOO$$

$$(3)\quad HCOO^- + OH \text{ (or H)} \longrightarrow CO_2^- + H_2O \text{ (or } H_2\text{)}$$

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$$(4)\quad CO_2^- \quad + \quad HCOO^- \longrightarrow [COO^-.OCH.O^-]$$

$$(5)\quad [COO^-.OCH.O^-] + CO_2 \longrightarrow COOH.COO^- + CO_2^-$$

In the following some preliminary ESR experiments on the formation of the intermediate ($COO^-.OCH.O^-$) radical ion in the radiolysis of the deaerated aqueous solutions of carbon dioxide, bicarbonate, carbonate, formic acid and formate, are reported.

ESR signals of the radicals formed in aerated water by ^{60}Co-γ-irradiation at 77°K have been interpreted as being due to OH and HO_2 radicals[8]. On warming the samples, the signals of the OH radical disappear between 90-110°K, those of the HO_2 radical at 145°K. In the case of frozen glycine solutions it has been shown that during warm-up the radicals react with the added solute to form secondary radicals[9]. ESR signals of the solvated electrons (e^-_{aq}) have been observed in strongly alkaline aqueous solutions[10].

In our experiments, 0.1 M solutions of A.R. grade chemicals in triply distilled water were used. Before freezing, the solutions were deaerated by purging with argon or carbon dioxide. The irradiation was carried out at 77°K for 1 - 2 hours (dose rate 1.1 Mrad/hour) in the ^{60}Co-γ-facility of our institute[11] with low temperature equipment designed for this purpose.

After irradiation the samples were quickly transferred under liquid nitrogen into the Dewar precooled variable temperature insert in the cavity of a Varian V-4500 EPR spectrometer (X-bd., 100 kc modulation). ESR spectra were then recorded as a function of temperature up to 250°K.

Solutions of formic acid. At 77°K the ESR signal (I) of the irradiated solutions proved to be identical with that of pure water. In formic acid, as well as in the other solutions described below, the signal (I) decayed rapidly between 85 - 95°K and simultaneously a new signal (II) was formed at higher field strengths. Signal (II) consisted of two components: (IIa) is a two-line signal with a 137 G splitting, which can be observed up to 120°K; this signal arises from CHO radicals. The second component (IIb) is an asymmetric single line with a width of 6.7 G between points of maximum slope and is observed up to 150°K (see fig. 1).

Solutions of sodium formate. In irradiated formate solutions essentially the same signal (II) was formed when the temperature was raised up to 120°K. The signal was stable up to 170°K and, with rising temperature, its intensity decreased slowly until it disappeared above 240°K. The intensity at 120°K was greater by a factor of 3 as compared to formic acid solution (see fig. 1). The single line (IIb) showed some indication of a small splitting. This could either be due to a very small hyperfine coupling or to the presence of two slightly different radicals.

Saturation of water, formic acid or formate solution with CO_2 at room temperature did not affect the intensity and temperature dependence of signals (I) and (II) after γ-irradiation.

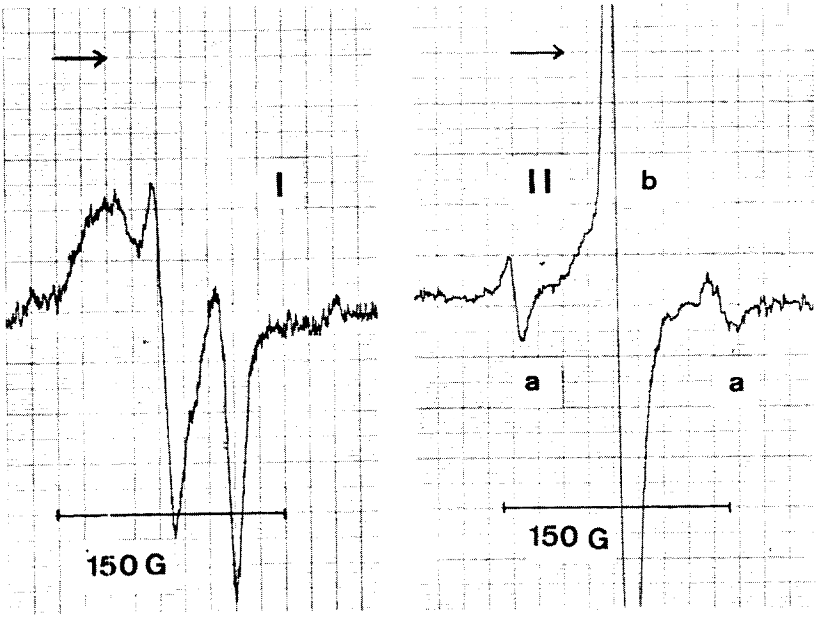

Figure 1: ESR spectra of irradiated solutions. I: 0.1 M formic acid at 77°K; II: 0.1 M sodium formate at 105°K.

<u>Formate solutions containing bicarbonate or carbonate</u>. Addition of sodium bicarbonate to a sodium formate solution did not influence the radical reactions in irradiated formate samples. In the presence of sodium carbonate the intensity of signal (IIb) after irradiation and warm-up to 120°K was increased by a factor of 4. Thus, the radicals primarily formed in water seem to react preferentially with the formate. This is borne out again by the fact that different radicals are formed in irradiated bicarbonate and carbonate solutions. At 77°K in both

cases the typical water-radicals were observed, however, on warming, another signal (III) developed at lower field strength than in formate solution, which disappeared at temperatures above 200°K. Signal (III) was an asymmetric single line, which seemed to split up into two components of different intensity and width above 120°K (see fig. 2).

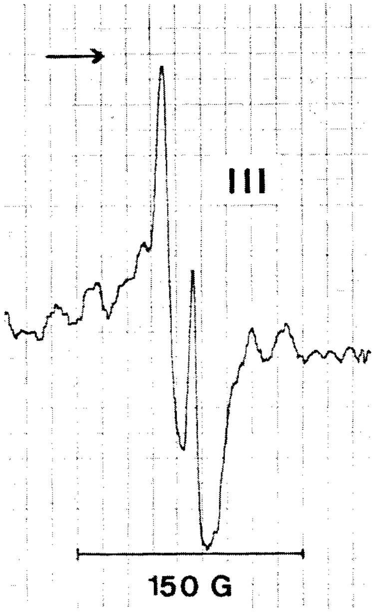

Figure 2: ESR spectrum of irradiated 0.1 M sodium carbonate solution at 120°K (III).

Recently, OH-radicals have been shown to react with formic acid in a chain process with HO_2 radicals being formed as precursors of the termination step[12]. ESR spectra of the radicals formed in irradiated pure formic acid at low temperature have been interpreted as CHO, CO_2H and HCO_2 radicals[13,14]. CO_2^-

radicals with the hyperfine splittings of the gegenions have been found in irradiated formate single crystals[15,16]. The CO_2H radical has also been observed in an irradiated potassium bicarbonate single crystal[17]. Recently Bellis and Clough[18] on heating irradiated formate single crystals to 180°C have observed the formation of the ($COO^-.OCH.O^-$) radical ion. Earlier, oxalate radicals were obtained in the low temperature photolysis of ferric oxalate complexes[19].

In interpreting our ESR spectra the following points may be considered:

1) From their position in the magnetic field and the change of their intensity with temperature we may positively conclude that the signals do not arise from HO_2 radicals. 2) The radicals of the solutes are not formed directly as a consequence of the irradiation but are products of a secondary reaction between the water radicals and the solute. 3) In our system formic acid behaves quite differently as compared to the pure substance[13,14]. In solution the intensity of signal (IIa) is much smaller than the intensity of signal (IIb) (whereas in pure formic acid their intensities are comparable). Furthermore, in pure formic acid two doublet hyperfine splittings of (IIb) have been reported[13,14], neither of these, however, could be observed in our experiments in frozen aqueous solutions.

Considering the reaction mechanism of radiation induced carboxylation of formic acid and formates[6,7] and the ESR experiments of Bellis and Clough[18] it occurs to us that our ESR results in frozen aqueous solutions point to the same radical intermediate, namely: ($COO^-.OCH.O^-$). In continuing this investigation with ^{13}C-labelled compounds and by other experiments we hope to ascertain our conclusions.

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