PHOTOLYTIC AND THERMAL ANNEALING OF RADICAL ANIONS IN GAMMA-IRRADIATED MONOCARBOXYLIC ACIDS

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Total yields of paramagnetic species, their optical bleaching and thermal annealing in acetic, propionic, n-butyric, isobutyric, and pivalic acid γ-irradiated at 77 K were followed by ESR spectroscopy. Radical anions, always found after irradiation, disappear during optical bleaching without formation of any paramagnetic product. During thermal annealing they are converted almost quantitatively into the α-radicals of the respective acid, with the exception of pivalic acid. Amounts of radical anions were estimated from the difference of integrated ESR spectra taken before and after optical bleaching. The results show that approximately equal amounts of the reduction and oxidation paramagnetic products of the γ-irradiation can be detected.

Electrons originating from the ionization acts during γ-irradiation are efficiently captured by carboxylic groups of aliphatic acids, and the corresponding radical anions can be detected by the electron spin resonance (ESR) spectroscopy at 77 K. The formation of the radical anions, was observed in a series of aliphatic monocarboxylic acids[1-3], in their perfluoro derivatives[4], in dicarboxylic acids, *e.g.*, in malonic acid[5], and succinic acid[6,7], and in all simple amino acids, *e.g.* in glycine[8], alanine[9,10], and α-aminobutyric acid[11,12].

In the case of acids with an α-carbon atom carying either three, two or one hydrogen atom, the ESR spectra of radical anions at 77 K consist of broad doublets with splitting 2·0–3·5 mT. The acids without any hydrogen on the α-carbon atom give only a broad signlet[13]. The splitting is due to the interaction of the unpaired electron of the carboxyl group with one hydrogen atom of the α-carbon atom. Correspondingly, in the perfluoro acids the doublet ESR spectra of the radical anions ($a \approx 5{\cdot}0$ mT) result from the unpaired electron interaction with one fluorine atom of the α-carbon atom of the acid[4]. The radical anions are suggested to be in the protonized form $(RCH_2COOH^-)H^+$ (refs[2,3,7,9,10,14,15]). The interaction of the unpaired electron with such a proton of the carboxylic group has been resolved by ESR only in the case of α-alanine[9,10,16] — in other cases such an interaction remains unresolved and contributes to the spectral line broadening.

The decay of the radical anions in monocarboxylic acids upon thermal annealing was proposed[2,3] to proceed according to equations (*A*) or (*B*):

$$RCH_2COOH^- \rightarrow RCH_2COO^- + H \qquad (A)$$

$$RCH_2COOH^- \rightarrow RCH_2CO + OH^- . \qquad (B)$$

The photolysis of γ-irradiated α-aminobutyric acid[11] and perfluorocarboxylic acids[4] at 77 K with ultraviolet light brought about the decay of the radical anions without their transformation into another paramagnetic species. However, in the case of glycine[17,18] the photolysis of the radical anion led to the formation of the $NHCH_2COOH$ radical.

The radical cations of acids, formed in the low temperature radiolysis, are generally accepted precursors of RCH_2 radicals detected by ESR at 77 K (refs[2,3,7,14,19-21]). The formation of RCH_2 radicals and CO_2 can be described by equations (*C*) and (*D*):

$$RCH_2COOH^+ + RCH_2COOH \rightarrow RCH_2COOH_2^+ + RCH_2COO^\bullet \quad (C)$$

$$RCH_2COO^\bullet \rightarrow RCH_2 + CO_2 . \quad (D)$$

Recently, the carboxylic radical could be detected by ENDOR measurement in succinic acid γ-irradiated at 4·2 K and its decomposition to RCH_2 radical was proved[20]. The lower amount of paramagnetic oxidation products found in succinic acid[7] was explained by the formation of another oxidation product — radical RCHCOOH differing structuraly from the ordinary radical arising from the decay of the radical anion[20].

In this study we follow quantitatively the photolytic and thermal annealing of radical anions and other paramagnetic species in γ-irradiated monocarboxylic acids with the aim to determine the amount of the radical anions. Since the radical anions are likely the only products of the reductive action of γ-irradiation at 77 K their quantitative determination could confirm the expected balance between oxidation and reduction products in γ-irradiated monocarboxylic acids.

EXPERIMENTAL

Acetic, propionic, n-butyric, isobutyric and pivalic acids were dried over the molecular sieve 5A, thereafter degassed *in vacuo* (10^{-5} Torr) and distilled into the Spectrosil silica tubes (diameter 4 mm) which were then sealed. Isobutyric acid formed a transparent glass at 77 K, while all the other acids were polycrystalline. The samples were irradiated in liquid nitrogen with ^{60}Co γ-rays at a dose rate of $5 . 10^{17}$ eV ml^{-1} min^{-1} with doses ranging from $3 . 10^{18}$ up to $5 . 10^{19}$ eV ml^{-1}.

The ESR spectra were recorded using an ESR X-band spectrometer (ER-9, Zeiss, Jena) provided with a 100 kHz magnetic field modulation and a simultaneous integrator. The derivative spectra were used for a qualitative analysis, the absorption spectra for a quantitative evaluation. For the sake of clarity, in this paper only the integrated spectra are presented. The areas of integrated spectra were measured using a planimeter and total radical yields were determined by a procedure described elsewhere[22]. The warming of irradiated samples was carried out in a stream of gaseous nitrogen of a required temperature, but the spectra were recorded always at 77 K. The samples were photolyzed at 77 K in a silica Dewar vessel by unfiltered light of a high-pressure HBO 200 mercury lamp.

Hydrogen was determined in the samples after the measurement of ESR spectra by gas chromatography. The gas from the irradiated sample was transferred into the sample loop by means of a Toepler pump[22].

RESULTS AND DISCUSSION

The derivative ESR spectra of γ-irradiated acids at 77 K and those after warming to higher temperatures agree qualitatively, unless, the difference is mentioned, with those published by Ayscough and coworkers[2,3]. Quantitative evaluation of results was carried out mainly with the aim to reveal the changes in radical concentrations accompanying both the photolytic and thermal annealing of radical anions and some following photolytic transformations of secondary radicals. The summary of the results together with total radical yields is given in Table I.

Acetic acid. The ESR spectrum of acetic acid γ-irradiated at 77 K is shown in Fig. 1. It consists of both the radical anion and the CH_2COOH radical spectra[22] in accordance with the recent single crystal study[23]. The previous observation of the radical anion spectrum only[2] was due to the partial microwave saturation of the ESR spectrum of CH_2COOH radical[22].

The radical anions are quite stable up to 130 K; at higher temperatures they are transformed quantitatively into CH_2COOH (Fig. 1).

Upon photolysis the radical anions rapidly disappear, and in 6 min only 53% of the initial radicals concentration remains. However, the shape of the spectrum indicates (Fig. 1) that the signal of the radical anion does no disappear completely. After another 14 min of photolysis the radical concentration decreases to 28% and the spectrum consists of the spectrum of CH_2COOH and of a broad central asymmetric band. This band is partialy similar to the spectrum of CH_3CO radical recorded by Bennett and coworkers[13], though neither the minor splitting due-to protons in the CH_3 group, nor a sample colouration were observed. Further photolysis increases the intensity of the central band on account of the signal of the CH_2COOH radical and the total spectrum intensity decreases only very slowly, to 20% after

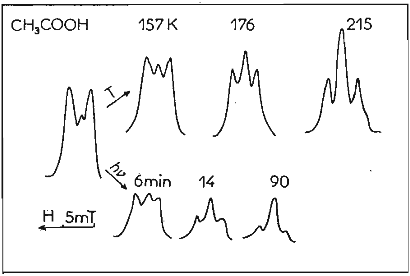

FIG. 1

Integrated ESR Spectra of Acetic Acid after Irradiation at 77 K and Thermal Annealing (*T*) or Optical Bleaching (*hν*)

TABLE I

Total Yields of Free Radicals, Amounts of Radical Anion, Photolytic and Thermal Annealing

Acetic acid; $G(R) = 4{\cdot}9$; 50 ± 5% of radical anion

$$\begin{bmatrix} CH_3COOH^- \\ CH_2COOH \end{bmatrix} \begin{array}{l} \xrightarrow{h\nu} (CH_2COOH + CH_3CO\ ?)\ 28\% \xrightarrow{h\nu} CH_3CO\ ? \\ \xrightarrow{195\,K} (CH_2COOH)\ 95\% \end{array}$$

Propionic acid; $G(R) = 6{\cdot}7$; 50 ± 5% of radical anion

$$\begin{tikzcd}[column sep=large]
\begin{bmatrix} CH_3CH_2COOH^- \\ CH_3CHCOOH \\ CH_3CH_2 \end{bmatrix} \arrow[r, "h\nu"] \arrow[dr, "108\,K"'] & (CH_3CHCOOH + C_2H_5)\ 49\% \arrow[dr, shift left, "195\,K"] & \\
& (CH_3CHCOOH + C_2H_5)\ 90\% \arrow[r, "130\,K"] & (CH_3CHCOOH)\ 81\% \arrow[ul, shift left, "h\nu"]
\end{tikzcd}$$

n-Butyric acid; $G(R) = 5{\cdot}4$; 50 ± 15% of radical anion

$$\begin{bmatrix} CH_3CH_2CH_2COOH^- \\ XCH_2CH_2CH_2 \\ \text{Other radicals} \end{bmatrix} \begin{array}{l} \xrightarrow{h\nu} (XCH_2CH_2CH_2 + CH_3CH_2CH_2CO\ ?)\ 55\% \\ \xrightarrow{130\,K} (XCH_2CH_2CH_2 + CH_3CH_2CH_2CO\ ?)\ 88\% \end{array}$$

i-Butyric acid; $G(R) = 5{\cdot}7$; 30% of radical anion

$$\begin{tikzcd}[column sep=large]
\begin{bmatrix} (CH_3)_2CHCOOH^- \\ (CH_3)_2CCOOH \\ (CH_3)_2CH \end{bmatrix} \arrow[r, "h\nu"] \arrow[dr, "90\,K"'] & ((CH_3)_2CCOOH + (CH_3)_2CH) 70\% \arrow[dr, shift left, "108\,K"] & \\
& (CH_3)_2CCOOH + (CH_3)_2CH \arrow[r, "108\,K"] & (CH_3)_2CCOOH\ 98\% \arrow[ul, shift left, "h\nu"]
\end{tikzcd}$$

Pivalic acid; $G(R) = 5{\cdot}2$; 50 ± 5% of radical anion

$$\begin{bmatrix} (CH_3)_3CCOOH^- \\ (CH_3)_3C \end{bmatrix} \begin{array}{l} \xrightarrow{h\nu} ((CH_3)_3CCOOH^- + (CH_3)_3C + (CH_3)_2CCOOH)\ 25\% \\ \xrightarrow{195\,K} \text{Simultaneous decrease of both radicals} \end{array}$$

90 min. The latter result agree with the qualitative observation of CH_2COOH behavior under photolysis[24].

The initial rapid decrease of the ESR spectrum intensity upon photolysis corresponds mostly to the radical anion disappearance. However, the actual yield of the radical anion at 77 K can be determined only by an indirect procedure, since in the initial period of photolysis the CH_2COOH radical is disappearing, too, and the extent of their transformation into another paramagnetic species is not known. Therefore, kinetics of photolysis of CH_2COOH radicals was followed at 77 K in irradiated acetic acid after a preliminary removal of the radical anions by thermal annealing at 195 K. It was found that the CH_2COOH radical concentration decreased by 21% during the initial 20 min period of photolysis. Provided that the presence of radical anions does not affect the photolysis of CH_2COOH radicals, the concentration of radical anions in γ-irradiated acetic acid at 77 K amounts to about 50% of all paramagnetic species.

In the radiolysis at 77 K, the precursor of CH_2COOH is probably the radical CH_3 originating in reactions (C) and (D). The photolysis of CH_2COOH in acetic acid does not result in trapping of CH_3 radicals as in similar compounds, *e.g.*, ammonium acetate[25], acetamide and hydrated sodium acetate[26]. Also, in a matrix of CH_3COOH containing H_2SO_4 the CH_3 radicals originating from CH_2COOH photolysis were trapped[24]. These observations show that the matrix of acetic acid is rather soft and it is not able to trap CH_3 radicals at 77 K.

The comparison of the results of photolytic annealing with those of thermal annealing indicates that in the first case the radical anions are removed without an appearance of another radical, while in the second case their quantitative transformation into CH_2COOH radicals occurs.

In addition to ESR spectra the radiation yields of hydrogen were determined after some annealing processes. The yield of hydrogen $G(H_2) = 2{\cdot}1$ was found in acetic acid γ-irradiated and photolyzed for 90 min at 77 K. The same yield was determined with the sample warmed to 195 K and photolyzed at 77 K for the same time. The irradiated non-photolyzed samples gave $G(H_2) = 0{\cdot}26$ in accord with the literature data[2].

Propionic acid. The ESR spectrum recorded after the irradiation of propionic acid at 77 K is shown in Fig. 2. It consists of the doublet of radical anion ($a = 2{\cdot}6$ mT), the anisotropic spectrum of C_2H_5, and a small contribution of the isotropic quintet of $CH_3CHCOOH$. The spectrum of the radical anion disappears completely within 3 min photolysis, while that one of C_2H_5 does not change; the total intensity of the ESR spectrum decreases to 49%. Further photolysis for 10 min diminishes the total spectrum intensity by 4% only and, simultaneously, some of the $CH_3CHCOOH$

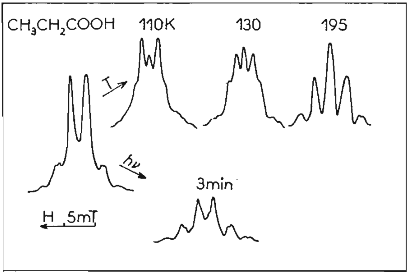

Fig. 2

Integrated ESR Spectra of Propionic Acid after Irradiation at 77 K and Thermal Annealing (T) or Optical Bleaching ($h\nu$)

radicals are transformed into C_2H_5 radicals. The concentration of the radical anion formed by the radiolysis at 77 K, calculated from the difference between the spectrum intensities before and after the photolysis, amounts to about 50% of the total radical yield. Warming of the photolyzed sample to 195 K causes the transformation of the ethyl radical to $CH_3CHCOOH$ by the hydrogen abstraction from the neighbouring acid molecule. At the same time the total spectrum intensity decreases to 34% of its initial value.

As far as the thermal annealing is concerned, the spectrum of the radical anion disappears completely as early as at 110 K and the spectrum of $CH_3CHCOOH$ appears; the total radical concentration decreases to 90%. When the sample was warmed to 130 K, only the spectrum of $CH_3CHCOOH$ with the intensity of 81% of the initial value was observed. Further warming to 195 K decreased the spectrum intensity to 51%.

The radical $CH_3CHCOOH$ can be transformed to the ethyl radical by a prolonged photolysis at 77 K and the latter can be converted back to $CH_3CHCOOH$ by warming the sample to 195 K. The loss in the total radical concentration in such a cycle amounts to about 10%. These photolytic and thermal radical transformations can be repeated many times.

In the irradiated propionic acid photolyzed for 30 min at 77 K the hydrogen yield $G(H_2) = 1{\cdot}3$ was determined. The irradiated samples warmed to 130 K and 195 K gave after the subsequent identical photolysis the yields of hydrogen equal to 1·1 and 0·6, respectively. These values are in a linear correlation with the amounts of radicals in the samples before the photolysis. The hydrogen yield from the irradiated non-photolyzed sample amounted to 0·28.

n-*Butyric acid*. The ESR spectrum observed after the sample irradiation (Fig. 3) consists of a broad doublet ($a = 2{\cdot}7$ mT) of the radical anion and of the complex

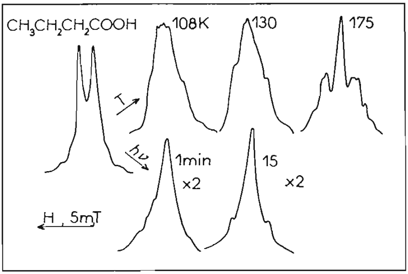

FIG. 3

Integrated ESR Spectra of n-Butyric Acid after Irradiation at 77 K and Thermal Annealing (*T*) or Optical Bleaching (*hν*) spectra of alkyl radicals. During the sample, photolysis both concentrations of the radical anion and of alkyl radicals diminish rapidly. The total spectrum intensity decreases to 74% and 55% after 30 s and 1 min photolysis, respectively, and the doublet of radical anion disappears completely. After 15 min of photolysis, the spectrum intensity decreases to 43% and the remaining spectrum is characterized by a broad singlet ($g = 2{\cdot}0006$) and a sharp doublet split 6·7 mT. The doublet probably corresponds to the $CH_2CH_2CH_2X$ radical ($X = COOH$ or H) identified formerly in a γ-irradiated single crystal of α-aminobutyric acid and in its polycrystalline matrix[11]. The isotropic doublet arises from the interaction of two different but nearly isotropic H_β protons with two anisotropic but equivalent H_α protons ($M_I = 0$ transitions).

The shapes of the ESR spectra indicate that the $CH_2CH_2CH_2X$ radical was present as early as in the γ-irradiated sample, similarly as in α-aminobutyric acid[11] and was not produced by the photolysis. The singlet signal arises on the account of other alkyl radicals disappearing during photolysis.

Thermal annealing of the γ-irradiated sample led to a significant decrease of the intensity of the radical anion doublet at 108 K and to its complete disappearance at 130 K. Simultaneously, the intensity of the doublet ($a = 6{\cdot}7$ mT) characteristic of $CH_2CH_2CH_2X$ increased; the total spectrum intensity decreased to 88%. The warming of the sample to 175 K caused an appearance of a singlet at $g = 2{\cdot}0006$ corresponding probably to the acyl radical, accompanied by alkyl radicals spectra; the total spectrum intensity decreased to 50%. After warming of both the photolytically and thermally annealed samples to 240 K the spectrum of an alkyl radical identical with that observed by Ayscough[3] appeared in the 6% intensity of the original value in both cases.

The amount of the radical anion in irradiated *n*-butyric acid cannot be determined accurately, since both radical anion and alkyl radicals disappear simultaneously

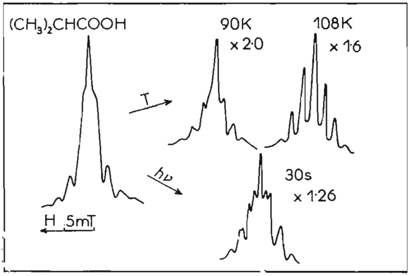

FIG. 4

Integrated ESR Spectra of Isobutyric Acid after Irradiation at 77 K and Thermal Annealing (*T*) or Optical Bleaching (*hν*) under the photolysis. We can anticipate, that the estimate of 50% for the concentration of the radical anion will not differ from the true value by more than ±15%.

Isobutyric acid. In the ESR spectrum observed immediately after the sample irradiation (Fig. 4) three components can be distinguished. The strongest one is formed by a septet (a = 2·13 mT) with binomial intensities distribution; the next one is a broad doublet (a = 2·3 mT) and the weakest one is an octet with the outermost bands shape typical for the H_α splitting. The spectra of the components were assigned to $(CH_3)_2\dot{C}COOH$, the radical anion and the $(CH_3)_2\dot{C}H$ radical, respectively.

After 30 s of photolysis the doublet of the radical anion disappeared, while the septet and the octet did not change; the total spectrum intensity decreased by 30%. The following warming of the sample to 108 K induced the transformation of the $(CH_3)_2\dot{C}H$ radical into $(CH_3)_2\dot{C}COOH$ by the abstraction reaction and at 130 K the latter disappeared slowly, too. The photolysis at 77 K of the sample thermally annealed at 108 K led to the partial development of the spectrum of $(CH_3)_2\dot{C}H$; however, even after a long lasting photolysis its intensity did not exceed 10% of the intensity of the $(CH_3)_2\dot{C}COOH$ spectrum. Moreover, a singlet with g = 2·0006 belonging apparently to an acyl radical appeared after a prolonged photolysis.

What concerns the thermal annealing of the γ-irradiated acid, the doublet of the radical anion disappears completely after one day at 77 K and the octet intensity decreases markedly. At 90 K the doublet disappears as early as after one hour and warming to 108 K causes the disappearance of the octet, too, but the total spectrum intensity remains unchanged. Thus, both the radical anion and $(CH_3)_2\dot{C}H$ change quantitatively into the $(CH_3)_2\dot{C}COOH$ radical at temperatures much lower than the corresponding transformations in other acids; it shows that the glassy matrix of isobutyric acid is very soft.

Pivalic acid. After sample irradiation at 77 K the ESR spectrum (Fig. 5) consisting of an isotropic decet with binomial intensities (a = 2·25 mT) and a broad

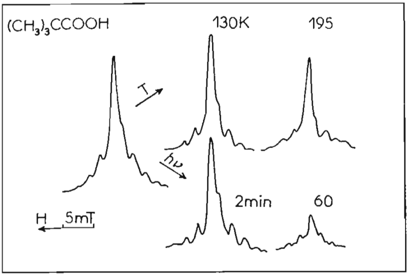

FIG. 5

Integrated ESR Spectra of Pivalic Acid after Irradiation at 77 K and Thermal Annealing (*T*) or Optical Bleaching (*hν*) singlet with $g \approx g_e$ was detected. The former signal corresponds to the $(CH_3)_3C$ radical and the latter to the signal of radical anion, since an acyl radical should have $g < g_e$. When the sample was photolyzed, the singlet diminished somewhat faster than the decet, and simultaneously a weak spectrum with odd number of lines appeared. The last spectrum is most likely the septet of the $(CH_3)_2CCOOH$ radical. After warming the photolyzed sample to 195 K the septet signal disappeared and the singlet intensity diminished further.

Since the rates of the photolytic removal of both the radical anion and the alkyl radical were comparable, it was not possible to determine the amount of the radical anion by the same procedure as with other acids. The amount of the radical anions present after γ-irradiation at 77 K was determined graphically as a difference between the total spectrum and the spectrum of $(CH_3)_3C$, assuming that the sample did not contain significant concentration of other radicals. According to this method the radical anions amounted to about 50% of the total radical concentration.

The thermal annealing of the irradiated sample brought about the decrease of intensities of both the decet and the singlet signals without appearance of another paramagnetic species.

CONCLUSIONS

In the monocarboxylic acids studied the following types of radical products were formed after the irradiation at 77 K: *a*) Radical anions produced by a capture of an electron by the carboxyl group, amounting to about 50% of the total concentration of all paramagnetic species; smaller amount of the radical anion found in isobutyric acid is apparently a consequence of its lower thermal stability in a glassy matrix. *b*) Radicals obtained by the decarboxylation of the radical cations according to equations (*C*) and (*D*) (exception – acetic acid). *c*) Radicals carrying a free valence on the α-carbon atom of acids (exception – pivalic acid). These radicals were formed according to reactions (*C*) and (*D*) followed by the abstraction reaction (*E*):

$$RR'CH + RR'CHCOOH \rightarrow RR'CH_2 + RR'CCOOH \quad (R' = CH_3 \text{ or } H) \qquad (E)$$

In the very soft matrix of isobutyric acid the latter radicals were formed by the reactions of the radical anion, too.

Upon thermal annealing, the radical anions changed more or less quantitatively into the RR'CCOOH radicals. The only exception occurred in the case of pivalic acid, where both the radical anion and the alkyl radical disappeared simultaneously.

The photolysis of all γ-irradiated acids at 77 K brought about the fast decay of the radical anions without formation of other radicals. In addition to this process the radicals RR'CCOOH were also partially disappearing in acetic, n-butyric and pivalic acid. In propionic acid the radicals RR'CCOOH were photolytically transformed into RR'CH radicals with high efficiency; in isobutyric acid the same process led to only a low concentration of RR'CH radicals whose thermal stability was limited at 77 K.

The hardness of the matrix and the stability of radicals play an important role in the annealing processes. Isobutyric acid, forming a glass at 77 K is the very soft matrix as both the radical anions and relatively stable RR'CH radicals decay at 77 K. In acetic acid the fast decay of the methyl radicals is due to their high reactivity in a likely not very hard matrix. Also, the formation of probably acyl radicals in both annealing processes (acetic, n-butyric and isobutyric acid) as well as the high effectiveness of the radical conversions $CH_3CHCOOH \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} CH_3CH_2$ in propionic acid can be related to properties of matrices.

Mechanisms of Annealing of Radical Anions

A simple thermal dissociation of protonized radical anions into the acid molecule and a hydrogen atom shown by reaction (*F*), analogous to reaction (*A*) cannot be assumed because the hydrogen yields obtained after the thermal annealing (0·26 and 0·28 for acetic and propionic acid, respectively) are much smaller than the yields of radical anions (being between 2·5 and 3·3 in all acids, see $G(R)$ in Table I).

$$RCH_2\bar{C}(=O)OH...H^+ \rightarrow RCH_2C(OH)_2 \rightarrow RCH_2COOH + H \qquad (F)$$

As the thermal annealing results in the transformation of radical anions into the acid radicals with a free valence on the α-carbon atom, either the existence of another reactive intermediate (hydroxyl or acyl radical) which reacts with the acid molecule without yielding hydrogen can be anticipated (equations (*G*) and (*H*)) or a direct reaction of the radical anion with another molecule of the acid (equation (*I*) can be suggested.

$$\begin{array}{lll} & \xrightarrow{\hspace{2em}} RCH_2CHO + OH & (G) \\ RCH_2\bar{C}(=O)OH...H^+ & \xrightarrow{\hspace{2em}} RCH_2CO + H_2O & (H) \\ & \xrightarrow{+RCH_2COOH} RCH_2CHO + H_2O + RCHCOOH & (I) \end{array}$$

The reaction pathway according to equation (*H*) was proposed in the case of succinic acid – the protonized radical anion in the form of a neutral radical $RCH_2C(OH)_2$ and an acyl radical were detected by ENDOR technique[14]. In all cases radicals of the type RCHCOOH should be formed in hydrogen abstraction by acyl or hydroxyl radicals.

The photolytic annealing of radical anions not yielding another paramagnetic products at 77 K is very peculiar. The direct photolytic decay of protonized radical anions via either the reaction (*J*) or (*K*) is very improbable.

$$\mathrm{RCH_2C(OH)_2} \xrightarrow{h\nu} \mathrm{RCH_2COOH} + \mathbf{H} \qquad (J)$$

$$\mathrm{RCH_2C(OH)_2} \xrightarrow{h\nu} \mathrm{RCH_2COH} + \mathbf{OH} \qquad (K)$$

This is because the (rather low) hydrogen yield is not influenced by the presence or absence of the radical anions in photolyzed samples of irradiated acetic and propionic acid, and the hydroxyl radicals or the secondary radicals, *e.g.*, RCHCOOH formed *via* the hydrogen abstraction by hydroxyl radicals[27] are not arising during photolysis. The diffusion and the complete recombination of hydroxyl radicals at 77 K is very improbable.

However, an intermolecular low temperature (4·2 – 77 K) transfer of electrons captured as radical anions in irradiated glycine hydrochloride has been observed[28]. It was also observed that free radicals, containing an oxygen atom in the neighbourhood of the free valence, could serve as trapping centers for electrons[29]. Therefore a suggestion can be made that the electron released from the radical anion by ultraviolet light (e_m^-) can be trapped by another protonized radical anion forming so a negatively charged but non-paramagnetic intermediate complex which can decompose, *e.g.*, according to equation (*L*).

$$\mathrm{RCH_2C(OH)_2} + e_m^- \overset{h\nu}{\rightleftharpoons} [\mathrm{RCH_2C(OH)_2}]^- \rightarrow \mathrm{RCH_2CHO} + \mathrm{OH^-} \qquad (L)$$

The released electrons are trapped selectively by the radical anions only, as the total concentrations of other radicals do not change considerably by photolysis at 77 K. This property of radical anions arises probably from the presence of oxygen atoms stabilizing the transient formal five-valent state of the carbon atom.

The observed balance between radical anions and radicals obtained from corresponding radical cations together with the theory of the photolytic decay of radical anions likely imply that the fast electrons originating in ionization acts do not react considerably with already formed radical anions and that the light emitted during irradiation does not affect observably the concentration of the radical anions.

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