

ELECTRON SPIN RESONANCE STUDIES OF γ -RADIOLYSIS OF α -AMINO BUTYRIC ACID

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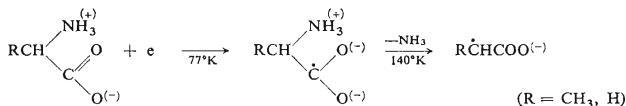
Dedicated to the 65th anniversary of the late Academician R. Brdička.

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Polycrystalline samples and single crystals of α -aminobutyric acid and D_3 - α -aminobutyric acid were irradiated at 77°K, then either gradually heated up or photolyzed, and their electron spin resonance spectra were measured. Analysis of these spectra showed that at 77°K in addition to the radical-anion $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{H}(\text{NH}_3^+)\dot{\text{C}}\text{OO}^{2-}$ further alkyl radicals $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$ and $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3^+)\text{COO}^-$ were formed. The radical-anion disappeared during the photolysis at 77°K without giving rise to another paramagnetic particle. Upon heating the sample, this radical decomposed presumably to the unstable radical $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCOO}^-$ which then — during further heating — gave rise to the stable radical $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3^+)\text{COO}^-$. The radical $(\text{CH}_3)_2\dot{\text{C}}\text{CO}^-$ was formed on the expenses of the latter radical at 100°C, but disappeared at 150°C and a new radical was formed which was not identified. The question of determination of products of oxidative effects of radiolysis is discussed in connection with the occurrence of the radical $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$.

Mechanism of radiolytic decomposition of simple α -aminoacids was studied in detail by means of the electron spin resonance (ESR) spectroscopy of both polycrystalline samples and single crystals. In order to obtain information on the radiolytic decomposition processes, aminoacids were irradiated by γ -rays or X-rays at low temperatures, where the primary products formed by high energy radiation are sufficiently stable. The samples were then gradually heated up, and further conversion of the products carrying an unpaired electron was followed by means of the ESR method.

From radiolytic products of glycine and α -alanine formed by irradiation at 77°K, only radical-anions were found by ESR having the unpaired electron on the carbon of the carboxyl group¹⁻³. Further conversions of these radical-anions were followed upon heating the samples; these concern their decomposition accompanied by deamination^{2,4-7}:



In the case of glycine the radical $\dot{\text{C}}\text{H}_2\text{COO}^-$ reacts by hydrogen abstraction with an adjacent molecule to form the stable radical $(\text{NH}_3^+)\dot{\text{C}}\text{HCOO}^-$ (see⁷). This mechanism holds also for decomposition of the radical-anion of α -aminoisobutyric acid and L-lysine hydrochloride from which stable radicals $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$ and $\text{NH}_2(\text{CH}_2)_3\dot{\text{C}}\text{HCOO}^-$ were formed, respectively, after deamination⁸.

On the other hand, paired primary products of oxidative effects of radiation, *i.e.* radical-cations and their decomposition products, have been observed by ESR spectroscopy in a few cases only. Thus, it was found that during irradiation of glycine hydrochloride the electron holes formed were located on Cl^- ions, and Cl atoms thus evolved reacted with further Cl^- to give stable Cl_2^- ions observed by the ESR technique⁹. However, attempts to find the oxidation products of glycine radiolysis at 4·2°K by means of ESR and the electron-nuclear spin double resonance method failed, though oxidative products were identified in dicarboxylic acids in thiourea derivatives, and in organic disulphides¹⁰.

The aim of this work was to identify the weak bands observed earlier^{5,6} in branches of the spectrum of the radical-anion in polycrystalline α -aminobutyric acid irradiated at 77°K, in particular to gather information on whether they may belong to the spectrum of the radical-cation. The study ought to show, whether the mechanism of radiolysis of aminoacids with a longer aliphatic chain is similar to that one for the lowest homologues. Last but not least, information on whether the photolysis of the primary radical-anions (radical-cations) influences the yield of radicals and which radicals are formed in it, may be of fundamental importance in biochemistry and radiation chemistry.

EXPERIMENTAL

Materials

DL- α -aminobutyric acid was obtained from B. D. H., Ltd., London and from Lachema, Brno. The exchange of the active hydrogens in the NH_3^+ group for deuterium was achieved by crystallization from 98·6% D_2O . Single crystals were prepared by slow crystallization from water or from heavy water. Crystals of the shape as shown in Fig. 1 were used in the experiments; some of them were elongated in the direction of the *a*-axis.

Measurements

Both polycrystalline samples and single crystals were sealed in *vacuo* into high purity quartz ("Spectrosil") tubes. The tubes for single crystals were preshaped in such a way that the crystals were fixed in them in required positions. The single crystals were rotated about the mutually

perpendicular axes a and b in the magnetic field (see Fig. 1). The samples were irradiated at 77°K by a ^{60}Co source (intensity 9.10^{17} eV/ml minute) for 1–3 hours according to the size of the sample. Photolysis of the irradiated samples was carried out by means of a high pressure mercury lamp whose short wave length radiation was filtered away by a glass plate 0.4 cm thick. Preliminary measurements of the ESR spectra in the X-band were carried out using the Decca Radar X-2 spectrometer with the 100 kc modulation, equipped with the 7" electromagnet (Newport Instruments) and a proton magnetometer for magnetic field calibration. Otherwise, the JES-3B ESR spectrometer (J.O.E.L. Co., Tokyo) was used in the measurements. During the measurements the samples were submerged in liquid nitrogen in a Dewar flask placed in the spectrometer cavity. Heating up of the samples was achieved by placing them into a bath of a melting organic substance previously cooled to its freezing point by liquid nitrogen. The following substances were used as the baths: light petroleum (b.p. 60°C), methanol, chloroform, carbon tetrachloride, and water. Water and oil baths were used to heat up the samples to temperatures above the room temperature. The ESR spectra were measured either at room temperature or at 77°K.

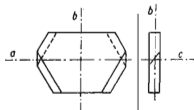


FIG. 1
A Well Developed Crystal of α -Aminobutyric Acid (Plan View and Side View)

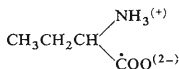
RESULTS AND DISCUSSION

ESR Spectra at 77°K after Irradiation

Polycrystalline samples of α -aminobutyric acid and D_3 - α -aminobutyric acid gave after irradiation at 77°K ESR spectra consisting of a very strong singlet in the middle, a much weaker doublet separated by 64 G, and a very weak unresolvable part of the spectrum of the total width of about 136 G (see Fig. 2A). Non-deuterated samples gave a somewhat broader singlet and slightly different shape of the branches.

Using of deuterated and non-deuterated single crystals resulted in approximately similar spectra: besides the strong central band split into a doublet 2–9 G, and a doublet 60–67 G (exhibiting a slight angular dependence when rotated around the a -axis), further strongly anisotropic signals were observed both inside and outside of the outer doublet (Fig. 3A). However, many fine bands separated often by only a few gauss observed in the non-deuterated crystal disappeared in the deuterated crystal.

The central singlet in the spectrum of the polycrystalline samples which was resolved into the doublet when single crystals were used, was ascribed to the radical-anion^{5,6}.



The doublet splitting reflects the interaction of the unpaired electron with the hydrogen on the α -carbon of the acid (spectroscopically the β -carbon). The exchange of the active hydrogens for deuterium manifests itself often in a mere narrowing of the bands and in a better resolution, as the resolved interaction of the unpaired electron with the active hydrogens was not observed^{1,5,8} with the exception of α -alanine^{2,3}.

Photolysis of the Products of Radiolysis at 77°K

Identification of the other radicals contributing to the spectrum was possible only after photolysis of the irradiated single crystal at 77°K was carried out. The photolysis

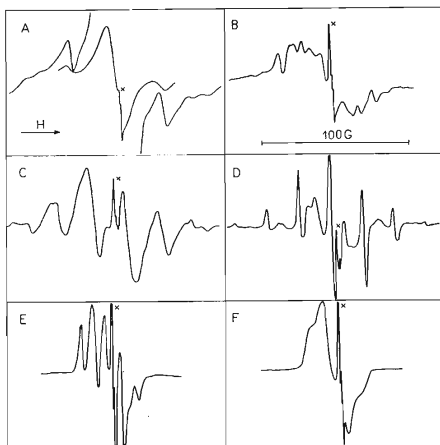


FIG. 2

ESR Spectra of Polycrystalline D_3 - α -aminobutyric Acid

A after irradiation at 77°K; B after heating up to -160°C (measured at 77°K); C after heating up to -60°C (measured at 77°K); D after heating up to 100°C (measured at room temperature); E after heating up to 150°C (measured at room temperature); F same as E, measured at 77°K. Samples heated for one hour. \times Signal of electrons in quartz.

was made by light of the wave-length longer than 300 m μ which does not cause photolytic changes in α -aminobutyric acid as proved by a blank experiment.

The photolysis bleached the spectrum of the radical-anion as well as many fine signals observed in the branches of the spectrum of the non-deuterated samples. However, the photolysis did not influence those bands that determined the maximum width of the spectrum prior to the photolysis, and the isotropic doublet 60–67 G as well as the corresponding anisotropic signal (compare Fig. 3A, 3B; see Fig. 4). The stronger spectrum characterized by the doublet 60–67 G already before the photolysis consisted of four triplets 1 : 2 : 1. The quartet of the bands of equal intensity which formed the middle of the triplets was rather isotropic (outer doublet 60–67 G, inner doublet 9–12 G). However, the triplet splitting was strongly anisotropic (from 17.6 G to 28.4 G) towards rotation around the a -axis. This spectrum may result from the interaction of the two H_{β} with $a_{\beta_1}^H = 25-28$ G and $a_{\beta_2}^H = 35$ to 40 G, and the two equivalent H_{α} with $a_{\alpha_{1,2}}^H = 17.6-28.4$ G. Only the radical $\dot{C}H_2CH_2CH(NH_3^+)COO^-$ can fit these data. It follows from interpretation of the spectrum that the bond C_3-C_4 in the acid is rigid and lies in the plane of the radical.

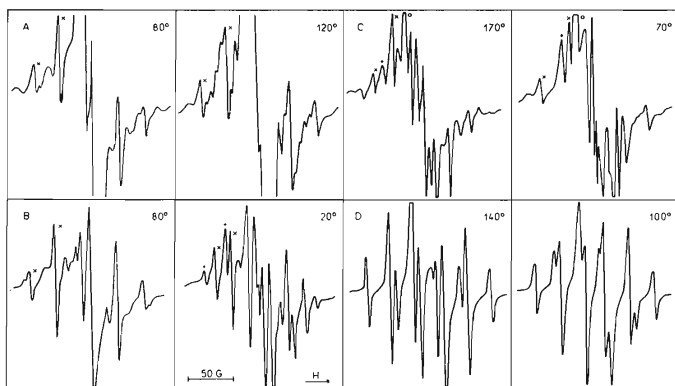


FIG. 3

ESR Spectra of Single Crystals of α -Aminobutyric Acid

A After irradiation at 77°K; B after photolysis at 77°K; C after heating up to -160°C (measured at 77°K); D after heating up to -98°C (measured at 77°K). Scales in figures give the position of the crystal (in degrees) during rotation around the a -axis and with respect to the magnetic field (at $0^{\circ} b \parallel H$). \times $\dot{C}H_2CH_2CH(NH_3^+)COO^-$ bands; $+$ $CH_3\dot{C}HCH(NH_3^+)COO^-$ bands; \circ $CH_3CH_2\dot{C}HCOO^-$ bands.

Thus, two different isotropic values a_{β}^H were found, as the extent of interaction of the H_{β} proton depends solely on the mutual orientation of the direction of the unpaired electron orbital and of the C—H bond. The rigid part of the radical, $\dot{C}H_2CH_2-$, as a whole must, however, keep reorienting itself quickly about the C_3-C_2 bond so that the two H_{α} atoms might be magnetically equivalent. A similar case of the motion of the n-propyl radical trapped in the argon matrix at 4.2°K was described by Cochran, Adrian and Bowers¹¹. In this case it is not certain if reorientation concerns the $\dot{C}H_2-$ group with respect to the CH_3CH_2- group or if it concerns the reorientation of the $\dot{C}H_2CH_2-$ having the H_{β} located in magnetically equivalent positions with respect to the p -orbital of the unpaired electron. However, it follows from comparison with the spectra of the same radical prepared by different methods^{12,13} that configuration and properties of the matrix substantially influence the structure of the radical and its mobility. On the other hand, in the CH_2 -group of the radical $\dot{C}H_2COO^-$ formed in the radiolysis of $Zn(CH_3COO)_2 \cdot 2 H_2O$ the reorientation motion begins above $-100^{\circ}C$ and at $95^{\circ}C$ the H_{α} -hydrogens appear to be magnetically equivalent and give the 1 : 2 : 1 triplet¹⁴. In view of all these facts, the hypothesis of rotation of the $\dot{C}H_2CH_2-$ group in a presumably not very densely packed matrix of α -aminobutyric acid appears to be acceptable.

The weaker spectrum determined the over-all width of the spectrum of the photolysed sample over the range 109–136 G upon rotation around the a -axis. Its outer

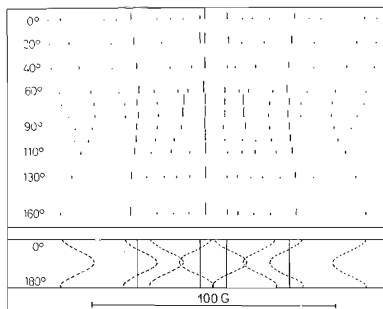


FIG. 4

Schematic Diagram of ESR Spectra of an Irradiated Single Crystal of α -Aminobutyric Acid Photolysed at 77°K when Rotated around the a -Axis

Only schematic spectra of the radical $\dot{C}H_2CH_2CH(NH_3^+)COO^-$ are given in the lower portion of the Figure. Solid lines — H_{β} splitting; dashed — H_{α} splitting.

bands were accompanied by a pair of bands separated from them by a roughly constant distance 23.5–26 G. The over-all width of the spectra as well as the isotropic splitting of the outer pair of bands exactly agreed with the data reported on the radical $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3^+)\text{COO}^-$ which is stable at room temperature. Its spectra were measured at 77°K, as discussed further on. Thus, the weaker spectrum can be reliably ascribed to this radical. In addition, there was a weaker singlet in the middle of the spectrum which remained after the photolysis and which was shifted by 6.4 G from the middle of the spectrum of the alkyl radical in the direction of the increasing field (Fig. 3B, 4).

Thermally Induced Conversions of Radicals

If the irradiated sample was heated up to -160°C , a very complicated spectrum resulted which consisted of the spectra of the radicals $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$ and $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3^+)\text{COO}^-$, and of a stronger anisotropic spectrum whose width varied between 50–33 G. The spectra thus obtained (Fig. 3C) were so complicated in the middle portion that an exact identification of the new, narrower spectrum was all but impossible. However, it was certain it did not originate in an interaction of more than three $\text{H}_{\alpha,\beta}$ hydrogens. It may be ascribed to the radical $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCOO}^-$ formed in deamination of the radical-anion, in a similar way as in the other amino-acids.

Upon heating of both this and the photolysed sample to -98°C and to higher temperatures, a simple anisotropic spectrum was obtained of the total width of 136–109 G upon rotation around the *a*-axis, and 134–114 G upon rotation around the *b*-axis. The spectra were composed of two almost isotropic quintets with binomial intensities whose mutual shift determined the anisotropic splitting of the H_α interaction (Fig. 3D). The splitting of the quintet varied between 23.5 and 26 G, the magnitude of the H_α interaction varied – upon rotation around the *a*-axis – between 14 and 33 G, upon rotation around the *b*-axis between 16.8 and 32.5 G. If $\text{H}_\alpha = \text{H}_\beta$, the spectrum coalesced into a sextet with a binomial distribution of the intensities. Upon rotation around the two mutually perpendicular axes the tensor of hyperfine interaction H_α reaches its maximum principal value and the values between the middle and the lowest principal values (around 20 G and 10 G, respectively). It follows then that the rotation axes thus chosen lie within the plane given by the C–H bond and by the direction of the unpaired electron orbital, and form with them an angle of about 45° . The only radical that exhibits the interaction of four equivalent H_β and of one H_α can be formed from α -aminobutyric acid by abstraction of the C_β hydrogen. Its structure is $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3^+)\text{COO}^-$. Similar radicals with the unpaired electron on the second carbon of the carbon chain have been found to be the main products of the γ -radiolysis of *n*-alkanes¹⁵: *n*-pentane up to *n*-decane single crystals give all radicals $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{R}$ when irradiated at 77°K. Spectra of these radicals consist

of an isotropic quartet $a_1 = 25 \pm 1$ G (CH_3), an isotropic triplet $a_2 = 33 \pm 1$ G (CH_2), and an anisotropic doublet $a_3 = 33 - 12.5$ G (H). In these cases the CH_3 group gives equivalent hydrogens and thus it rotates with respect to the carbon of the radical which is fixed; a similar phenomenon occurs in the radical found in α -aminobutyric acid. However, the magnetically symmetric position of the β -hydrogens in the CH_2 group is remarkable, as it does not occur in radicals prepared from alkylhalides^{12,13}. In the radical from α -aminobutyric acid one isolated β -hydrogen exhibits a splitting which is different from that one found in the hydrocarbon radicals: its splitting is equal to the splitting of H_β atoms of CH_3 group. Radicals formed by abstraction of one hydrogen in the terminal CH_3 group (similar to those found in α -aminobutyric acid at 77°K) were not detected in the radiolysis of hydrocarbons.

The radical $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3^+)\text{COO}^-$ in α -aminobutyric acid was stable up to 60°C. However, when the samples were heated to 100°C, this radical disappeared and a new radical emerged which gave an isotropic septet in binomial intensities (Fig. 2C, 2D). The splitting of the septet in single crystals varied within 21.7–22.4 G. This spectrum can be ascribed only to the rearranged radical $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$ or $(\text{CH}_3)_2\dot{\text{C}}\text{COOH}$. Here, similarly as in the radical $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3^+)\text{COO}^-$ at 77°K, the rotation of the CH_3 groups is so fast that their hydrogens appear as magnetically equivalent. Comparison of the extent of splitting of hydrogens in the CH_3 groups confirms a general rule that the splitting decreases with the number of CH_3 groups interacting with the electron. In the radicals $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$ or $(\text{CH}_3)_2\dot{\text{C}}\text{COOH}$ formed in α -isobutyric acid the splitting of the isotropic septets varies between 22 to 23 G (see¹⁶). After heating to 130°C another, narrower spectrum appeared in addition to the septet spectrum. At 150°C the septet completely disappeared and a new, slightly asymmetric spectrum with five lines and $g \approx 2.004$ (at room temperature) appeared in the polycrystalline samples (Fig. 2E). The spectra of single crystals at the same temperature were entirely similar to those of the polycrystalline samples: they showed five almost isotropic lines (upon rotation around the b -axis at $a \perp H$ possibly six lines) separated by 9–11 G from each other. When measured at 77°K, the lines of the spectrum of the polycrystalline substance coalesced to form a broad singlet preserving the blurred envelope of the spectrum as measured at room temperature (Fig. 2F). Measurements on single crystals at 77°K did not give spectra of a better resolution either. Thus this extensive widening of the bands has to be ascribed to a higher freedom in orienting radicals formed at such high temperatures within the matrix. A radical that gives this spectrum may contain a central nitrogen atom interacting with hydrogen, but the actual structure cannot be ascertained from the available data. It is very probable that this radical is a product of a complete destruction of the molecule.

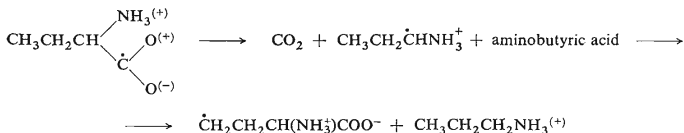
The spectra of the radicals as reported in this paper were for the most part not sensitive to the substitution of the active hydrogens by deuterium. Only in the case

of the radical-anion spectrum obtained by irradiation at 77°K, and in the case of the lastly mentioned radical formed at high temperatures, a certain narrowing of bands was observed after deuteration.

Sharp signals registered when measuring polycrystalline samples at 77°K which appeared in the middle of the spectra (Fig. 2) were due to electrons trapped in the quartz of the Dewar vessels during other experiments. Only a weak signal of electrons from the "Spectrosil" tube was observed when single crystals were measured at low temperatures.

MECHANISM OF RADIOLYTIC DECOMPOSITION

The radiolysis of α -aminobutyric acid at 77°K leads — similarly as in the case of glycine^{1,5-7,10}, α -alanine^{2,3}, and α -aminoisobutyric acid⁸ to the formation of the radical-anion in which the unpaired electron is located on the carboxyl carbon. In contrast to glycine and alanine, in α -aminobutyric acid in addition to the radical-anion substantial amounts of the radicals $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$ and $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3^+)\text{COO}^-$ are formed. Breaking of a C—H bond on the last-but-one carbon is a usual phenomenon in γ -radiolysis of hydrocarbons with a longer chain. However, breaking of a C—H bond in the terminal CH_3 group is rather unusual. In the case of α -aminobutyric acid this may be either a specific property of a longer hydrocarbon chain terminated by polar group or it may be due to the fact that this radical results from a radiolytic oxidative decomposition process. In the latter case, however, the radical should be a secondary product formed in a hydrogen abstraction process by the radical-cation from an adjacent molecule (the radical-cation is supposed to be short of one electron in the oxygen of the carboxyl group). The hydrogen abstraction could be preceded by the decarboxylation process and this would account for the presence of carbon dioxide among the products of α -aminobutyric acid radiolysis¹⁷. The radical $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3^+)\text{COO}^-$ could be in this case of the same origin, its lower abundance at 77°K might result from a crystal configuration less convenient for an abstraction of the H-atom from the β -carbon of an adjacent molecule by the radical-cation. One of the possible paths of the radical-cation decomposition is illustrated in the following schematics:



The fine structure observed in the branches of the spectrum of α -aminobutyric acid irradiated at 77°K and characterized often by a splitting of a few gauss only,

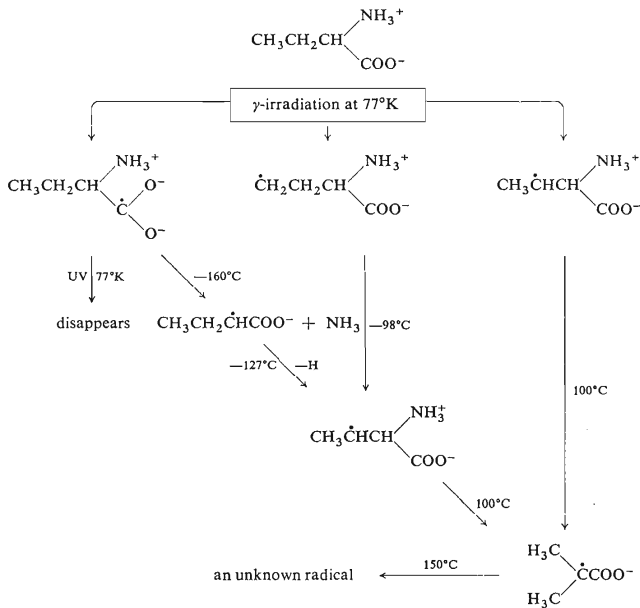
may indicate the presence of a radical similar to that one suggested by Fujimoto, Seddon and Smith⁸ to be formed in γ -irradiated aminoisobutyric acid at 77°K. They assumed that a weak anisotropic spectrum outside of the spectrum of the radical-anion was caused by $\text{RCH}(\dot{\text{N}}\text{H}_2^+)\text{COO}^-$ formed by abstraction of hydrogen from the NH_3^+ group of the acid.

Spectra of the radical-anion disappeared both when the samples were heated to -160°C and during photolysis at 77°K. On the contrary, spectra of the radicals $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$ or and $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3^+)\text{COO}^-$ did not change under these conditions. After heating the sample to -160°C , a stronger spectrum appeared in addition to the spectra of the two above mentioned radicals. It belonged presumably to the radical $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCOO}^-$ which would be formed by deamination of the radical-anion as a result of its thermal decomposition. Similar processes were observed in α -alanine^{2,4}, glycine⁷, and α -aminoisobutyric acid^{8,18}.

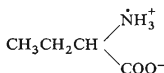
After completing the photolysis at 77°K, the over-all spectrum contained — besides the spectra of the two stable radicals — only a weak signal which might have been caused by electrons trapped in the quartz of the reaction vessel. This simplicity indicates that in the photolysis either the recombination between the radical-anion and the radical-cation took place, or a decomposition of the radical-anion occurred and the product with an unpaired electron disappeared quickly without forming any further radical products. If the alkyl radicals formed in irradiation at 77°K were products of the decomposition of the radical-cation, the first possibility would be excluded.

After heating the samples to -98°C or higher, all radicals are converted to one single radical $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{NH}_3)\text{COO}^-$ which originates in abstraction of hydrogen from adjacent molecules by other, less stable radicals. After heating the samples to -127°C the spectrum of the radical $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$ can be observed in addition to the above mentioned one. The former radical is very stable and only at 100°C its conversion occurs. The decrease of its concentration is then practically proportional to the increase of concentration of the radical $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$ which is formed either by an rearrangement of the parent radical or by the abstraction of NH_2^+ or NH_3^+ from an adjacent molecule and by a subsequent conversion to the most stable radical that can be formed with such a carbon skeleton. Isomerization of *n*-alkyls to branched radicals has not yet been observed in ESR spectra, though the tendency to form stable radicals with the maximum number of CH_3 groups was observed in a low temperature study of isomerization of isobutyl to tertiary butyl^{12,13}. Another radical found at 150°C is evidently a product of the decomposition of $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$ accompanied by a complete destruction of the molecule.

The mechanism of the radiolysis of α -aminobutyric acid can be described as follows:



The radical of a possible structure



was not included into the schematics as its structure is not certain and its fate during the radiolysis is not known. The schematics traces conversions and behaviour of those paramagnetic products of radiolysis that were stable at least at 77°K. Similarly as in the case of glycine^{4-6,9} and α -alanine^{2,4} the participation of paramagnetic intermediates in decomposition processes leading to decarboxylation was not proved, though the presence of the unusual radical $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$ may be explained — besides by the specific behaviour of the alkyl chain of α -aminobutyric acid — by its participation in the decarboxylation process. As the fate of the radical-anion and its decomposition products are well known to lead to deamination — as shown

in many ESR studies—it appears almost certain that the decarboxylation decomposition should be ascribed to reactions of the radical-cations.

Some of the preliminary measurements were performed in the laboratory of Dr P. B. Ayscough at the Leeds University. The author expresses his deep gratitude to Dr P. B. Ayscough for awarding him a position in the laboratory and for stimulating in him the interest in radiolysis of amino acids. The help of Dr A. Habersbergerová, Institute of Nuclear Research, Řež, in irradiating the samples as well as the help of Dr J. Pilař, Institute of Macromolecular Chemistry, Prague, in measuring the ESR spectra is gratefully acknowledged.

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