

PHOTOLYTIC AND THERMAL ANNEALING OF RADICAL ANIONS IN GAMMA-IRRADIATED AMMONIUM SALTS OF CARBOXYLIC ACIDS

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The γ -radiolysis of simple ammonium carboxylates at 77 K generates radical anions in yields comparable with those found in parent carboxylic acids. The structure of radical anions as derived from their ESR spectra and their behaviour on thermal annealing and photobleaching is mostly analogous to that found in carboxylic acids. The fast photobleaching of radical anions allowed to estimate the amount of radical anions in the sum of all paramagnetic products after γ -radiolysis. These amounts ranged usually 50%, only in ammonium acetate the unexplainable 75% of radical anions were found. Very efficient photolytic and thermal transformations of radicals $\text{R}\dot{\text{C}}\text{HCOO}^- \xrightleftharpoons[\Delta]{\text{UV}} \text{R}\dot{\text{C}}\text{H}_2$ were observed in ammonium acetate ($\text{R} = \text{H}$) while in the propionate ($\text{R} = \text{CH}_3$) both radicals decayed during photolysis.

ESR studies of paramagnetic species in γ -irradiated aliphatic monocarboxylic acids at low temperatures have contributed to the explanation of processes proceeding during radiolysis and during the thermal and photolytic annealing of radicals stabilized at low temperatures¹⁻⁴. Recently, the photobleaching property of the radical anions trapped in simple aliphatic acids upon γ -radiolysis at 77 K was established and the content of radical anions, about 50% of all paramagnetic species, was determined by quantitative ESR spectroscopy⁵. Similar studies with salts of aliphatic acids were restricted mainly to alkali metal acetates. In anhydrous alkali metal acetates irradiated at 77 K the $\dot{\text{C}}\text{H}_2\text{CO}^-$ radicals, sometimes accompanied by $\dot{\text{C}}\text{H}_3$ radicals, were always found by ESR method and the stability of CH_3 radicals at 77 K was dependent on the nature of alkali metal cation⁶. The presence of water of crystallization generally enhanced their stability⁷⁻⁹. The radiolytic damage in ammonium salts of aliphatic acids was studied by ESR only in ammonium acetate^{10,11} and ammonium trifluoroacetate¹². In the former case the ESR spectrum obtained after γ -radiolysis at 77 K was ascribed to the methyl radical exhibiting interaction with distant protons of matrix while in the latter case the assignment of the ESR spectrum to the radical anion was preferred.

In this paper, the paramagnetic species trapped in ammonium carboxylates after γ -irradiation at 77 K are thermally and photolytically annealed and their formation and annealing processes are followed by ESR spectroscopy. The nature of paramagnetic species and annealing processes are compared with those previously observed in parent carboxylic acids⁵.

EXPERIMENTAL

Ammonium salts of acetic, propionic, n-butyric, iso-butyric and pivalic acids were prepared by neutralization of acids with aqueous ammonia. Solutions were evaporated *in vacuo* and ammonium salts were purified by sublimation at 10^{-1} Pa and about 333 K. All ammonium salts were crystalline materials except ammonium n-butyrate which remained a viscous liquid. Crystals of salts were powderized and sealed in evacuated Spectrosil tubes. Single crystals of ammonium acetate were grown by slow sublimation *in vacuo*. They were fixed in positions corresponding to crystallographic axes. Sample irradiations, photolytic and thermal annealings and ESR measurements were carried out as described in the preceding study on carboxylic acids⁵. The first derivative and integrated ESR spectra were recorded simultaneously, the former for the qualitative, the latter for the quantitative evaluation of spectra. Amounts of radical anions stabilized at 77 K were estimated from the difference in the total amounts of paramagnetic species observed before and after photolysis of samples.

RESULTS AND DISCUSSION

Results obtained on photolytic and thermal annealing of radicals trapped in γ -irradiated ammonium carboxylates at 77 K are summarized in Table 1. Special features of processes proceeding in the particular salts are discussed separately.

Ammonium acetate. The γ -irradiated polycrystalline samples gave the ESR spectrum consisting of four broad lines in intensity ratio 1 : 6 : 6 : 1 with the splitting $a = 2.3$ mT (Fig. 1). After 30 s photolysis this spectrum disappeared and the remaining spectrum intensity decreased to 25% of the original value. This spectrum was composed of the quartet of narrow lines with intensity ratio 1 : 3 : 3 : 1 and $a = 2.25$ mT belonging undoubtedly to the methyl radical and of the anisotropic spectrum characteristic for the $\dot{\text{C}}\text{H}_2\text{COO}^-$ radical.

Upon thermal annealing at 130 K the original ESR spectrum was mostly substituted by the spectrum of $\dot{\text{C}}\text{H}_2\text{COO}^-$ radical. This process was accomplished by warming to 175 K and the pure polycrystalline spectrum of $\dot{\text{C}}\text{H}_2\text{COO}^-$ radical was obtained in the intensity corresponding to 91% of all paramagnetic species formed by γ -irradiation at 77 K. Further warming to 200 K did not change both, the line shape and the intensity of the spectrum. The lower intensity of the $M_1 = 0$ line in comparison with that observed in the spectrum of $\dot{\text{C}}\text{H}_2\text{COOH}$ in acetic acid^{2,5,13} can be explained either by slower reorientation of the CH_2 group in the acetate matrix or, more likely, by the presence of $\dot{\text{C}}\text{H}_3\text{CO}$ radical giving the single-line spectrum in the thermally annealed sample of acetic acid.

The $\dot{\text{C}}\text{H}_2\text{COO}^-$ radical obtained by thermal annealing to 200 K could be converted to the methyl radical by photolysis at 77 K; nearly total conversion was achieved after 5 min photolysis. When the sample was then warmed to 200 K the methyl radicals disappeared by the abstraction reaction giving rise to $\dot{\text{C}}\text{H}_2\text{COO}^-$ radicals. Total loss of radicals in such a cycle was about 5% only. These results show that the $\dot{\text{C}}\text{H}_2\text{COO}^-$ radicals observed in addition to methyl radicals in the γ -irradiated

TABLE I

Total yields of free radicals (G(R) in ammonium carboxylates γ -irradiated at 77 K, the amount of radical anions and photolytic and thermal annealing

$\left[\begin{array}{l} (\text{CH}_3\text{COONH}_4)^- \\ \dot{\text{C}}\text{H}_2\text{COO}^- \end{array} \right]$	Ammonium acetate; G(R) = 3.0; 75% of radical anion	$\xrightarrow{h\nu} [\text{CH}_3 + \dot{\text{C}}\text{H}_2\text{COO}^-] \xrightarrow{h\nu} \text{CH}_3$	25%
		$\xrightarrow{108\text{K}} [(\text{CH}_3\text{CONH}_4)^- + \dot{\text{C}}\text{H}_2\text{COO}^-] \xrightarrow{130\text{K}} \dot{\text{C}}\text{H}_2\text{COO}^-$	91%
$\left[\begin{array}{l} (\text{CH}_3\text{CH}_2\text{COONH}_4)^- \\ \text{CH}_3\dot{\text{C}}\text{H}_2 \\ \text{CH}_3\dot{\text{C}}\text{HCOO}^- \end{array} \right]$	Ammonium propionate; G(R) = 4.2; 50 \pm 10% of radical anion	$\xrightarrow{h\nu} [\text{CH}_3\dot{\text{C}}\text{H}_2 + \text{CH}_3\dot{\text{C}}\text{HCOO}^-]$	40%
		$\xrightarrow{108\text{K}} [(\text{CH}_3\text{CH}_2\text{COONH}_4)^- + \text{CH}_3\dot{\text{C}}\text{HCOO}^-] \xrightarrow{130\text{K}} \text{CH}_3\dot{\text{C}}\text{HCOO}^-$	98%
	Ammonium butyrate; G(R) = 4.7; 50 \pm 5% of radical anion		
$\left[\begin{array}{l} (\text{CH}_3\text{CH}_2\text{CH}_2\text{COONH}_4)^- \\ \dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{X} \\ \text{Other radicals} \end{array} \right]$		$\xrightarrow{h\nu} [\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{X} + \text{alkyl radicals}]$	50%
		$\xrightarrow{130\text{K}} [\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{O} + \text{CH}_3\dot{\text{C}}\text{HCH}_2\text{COO}^-]$	87%
$\left[\begin{array}{l} ((\text{CH}_3)_2\text{CHCOONH}_4)^- \\ (\text{CH}_3)_2\dot{\text{C}}\text{H} \\ (\text{CH}_3)_2\dot{\text{C}}\text{COO}^- \end{array} \right]$	Ammonium isobutyrate; G(R) = 4.4; 60 \pm 20% of radical anion	$\xrightarrow{h\nu} [(\text{CH}_3)_2\dot{\text{C}}\text{H} + (\text{CH}_3)_2\dot{\text{C}}\text{COO}^-]$	20%
		$\xrightarrow{130\text{K}} [(\text{CH}_3)_2\dot{\text{C}}\text{H} + (\text{CH}_3)_2\dot{\text{C}}\text{COO}^-]$	85%
	Ammonium pivalate; G(R) = 2.3; 50 \pm 10% of radical anion		
$\left[\begin{array}{l} ((\text{CH}_3)_3\text{CCOONH}_4)^- \\ (\text{CH}_3)_3\dot{\text{C}} \\ (\text{CH}_3)_2\dot{\text{C}}\text{COO}^- \end{array} \right]$		$\xrightarrow{h\nu \text{ or } 130\text{K}} \text{Simultaneous decay of all radicals}$	

sample after 30 s photolysis should be present even in higher concentration before photolysis. In analogous experiment with the sample irradiated at 77 K and warmed to 200 K, about 17% of $\dot{\text{C}}\text{H}_2\text{COO}^-$ radicals was replaced by methyl radicals after 30 s photolysis at 77 K.

The single crystal study was also performed on γ -irradiated ammonium acetate in an effort to find the reason for the large linewidth of the original spectrum. The four-line spectrum (approx. 1 : 4 : 4 : 1) showed small angle dependence of the hyperfine coupling ($a = 2.20 - 2.34$ mT) but the linewidth well observable on outer lines changed from 0.4 to 0.8 mT showing the additional doublet splitting at the maximum linewidth. The linewidth variation of the inner doublet could not be measured so exactly as it overlapped with weaker, strongly anisotropic spectrum of $\dot{\text{C}}\text{H}_2\text{COO}^-$ radical. After warming to 200 K the single crystal spectra showed that the $\text{CH}_2\dot{\text{C}}\text{OO}^-$ radical was the only paramagnetic species present.

These results are analogous to the ESR results obtained by Kispert and coworkers^{10,11} on X-irradiated single crystals of ammonium acetate at 77 K. They interpreted the ESR spectrum of four lines with varying linewidth as the spectrum of methyl radical being in interaction with distant protons of the matrix. The principal hyperfine couplings and direction cosines for protons of the methyl radical and for the closest matrix proton $a_1 = 0.47$ mT, $a_2 = 0.63$ mT, $a_3 = 0.89$ mT were determined by ELDOR measurement. The origin of this proton was established by the disappearance of the anisotropic splitting in the acetate containing deuterated ammonium group. The comparison of direction cosines for $\dot{\text{C}}\text{H}_3\text{—H}$ with the crystallographic molecular structure of ammonium acetate revealed that the methyl radical did not move more than 0.03 nm from

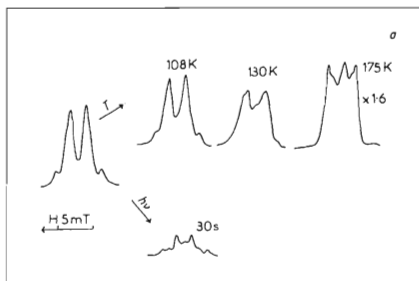


FIG. 1

Integrated ESR spectra of ammonium acetate (a) after γ -irradiation at 77 K and thermal annealing or (T) optical bleaching (hv)

its position in undamaged molecule and that the distance of one proton of NH_4^+ group to the unpaired electron was as low as 0.27 nm. Though these results allowed the interpretation of the spectrum as due to radical anion the authors rejected it because the hyperfine splitting ($a \approx 2.3$ mT) seemed to be much lower than that found in the radical anion of acetic acid ($a = 3.3$ mT).

We suggest that the photobleaching behavior of the radical giving the four-line ESR spectrum is indicative of the radical anion since all radical anions trapped in simple aliphatic acids⁵, aminoacids^{14,16} and aliphatic perfluoroacids⁴ could be bleached out by UV light. Also, the radicals trapped at 77 K in other ammonium carboxylates behave as the radical anions. The observed spectrum can be assigned to the radical anion having the rotating methyl group in α -position to the carboxyl carbon atom bearing the unpaired electron. The hyperfine splitting $a = 2.3$ mT is quite close to that observed in $\text{CH}_3\dot{\text{C}}\text{HCOOH}$ radical in propionic acid³ ($a = 2.37$ mT) or in $\text{CH}_3\dot{\text{C}}\text{HCOO}^-$ radical in α -alanine¹⁷ ($a = 2.5$ mT). The rotating methyl group of the radical anion should indicate that the matrix of ammonium acetate is rather soft as the rotation of methyl group of the radical anion is frozen in acetic acid² and it is hindered in the $\text{CH}_3\dot{\text{C}}\text{HCOO}^-$ radical in α -alanine at 77 K (ref.¹⁷). The different matrix structures of ammonium acetate and acetic acid are also reflected in the different behavior of $\dot{\text{C}}\text{H}_2\text{COO}^-$ and $\dot{\text{C}}\text{H}_2\text{COOH}$ radicals upon photolysis⁵. The suggestion that radical anion is formed in ammonium acetate is supported by results of the single crystal study on γ -irradiated ammonium trifluoroacetate at 77 K (ref.¹²). In this case the main products were radical anion and $\dot{\text{C}}\text{F}_2\text{COO}^-$ radical. The ESR spectrum of the radical anion appearing as a set of eight doublets was interpreted in terms of the frozen CF_3 group showing three inequivalent fluorine nuclei coupled with proton of the NH_4^+ group. The principal values of the proton coupling $a_1 = 0.65$ mT, $a_2 = 0.75$ mT, $a_3 = 1.41$ mT fall into the range observed in ammonium acetate¹⁰ and reflect so the close structural similarity of both compounds.

Ammonium propionate. The ESR spectrum shown in Fig. 2, observed after the sample irradiation at 77 K, consisted of components known from the study of γ -radiolyzed propionic acid: a doublet of the radical anion with $a = 2.7$ mT, characteristic spectrum of ethyl radical and a quintet of $\text{CH}_3\dot{\text{C}}\text{HCOO}^-$ radical⁵. After 3 min photolysis the doublet disappeared and the total spectrum intensity decreased to 40% of the original value. The remaining spectrum corresponded to a mixture of ethyl and $\text{CH}_3\dot{\text{C}}\text{HCOO}^-$ radicals. The further photolysis increased the relative amount of ethyl radical but the total radical concentration decreased. Thus the total decrease of radical species during the photolysis of the γ -irradiated sample cannot be accounted for the removal of radical anions only. By applying a correction for the simultaneous decrease of alkyl radicals concentration the estimate of the 50% concentration of radical anion in all paramagnetic species formed by γ -irradiation is obtained.

When the γ -irradiated sample was warmed to 108 K the doublet of radical anion was preserved, the ethyl radicals were replaced by $\text{CH}_3\dot{\text{C}}\text{HCOO}^-$ radicals by the hydrogen abstraction reaction and the total radical concentration did not change. At 130 K the marked decrease of the doublet intensity was balanced by the increase of $\text{CH}_3\dot{\text{C}}\text{HCOO}^-$ spectrum intensity so that the total radical concentration was not changed. After sample warming to 175 K only the spectrum of $\text{CH}_3\dot{\text{C}}\text{HCOO}^-$ with the intensity 63% of the original value was observed. Upon photolysis of this sample at 77 K the concentration of the radical decreased while that of ethyl radical increased but the total radical concentration decreased. The extended photolysis led only to a mixture of about equal amounts of both radicals.

Ammonium n-butyrate. After the sample irradiation at 77 K the ESR spectrum shown in Fig. 3 consisted of a doublet of broad lines $a = 2.7$ mT and a complicated spectrum of alkyl radicals; nearly the same spectrum was previously observed in n-butyric acid under the same conditions^{3,5}. The doublet of presumably the radical anion was largely removed by 90 s photolysis and simultaneously the total spectrum intensity decreased to 50%. Further, one hour photolysis resulted in slow transformations of alkyl radicals and a small diminution of the total spectrum intensity by 7%. In this spectrum, the presence of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{X}$ ($\text{X} = \text{COO}^-$ or H) radical characterized by sharp isotropic bands separated by 6.7 mT was identified; the same radical

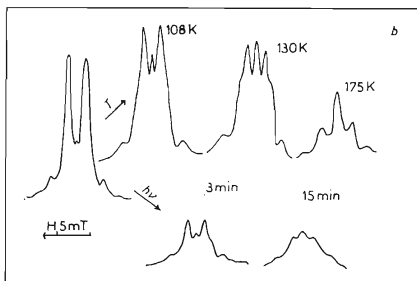


FIG. 2

Integrated ESR spectra of ammonium propionate (b) after γ -irradiation at 77 K and thermal annealing (T) or optical bleaching ($h\nu$)

has been observed in irradiated *n*-butyric acid⁵ and α -aminobutyric acid^{15,16}. A reliable identification of other radicals was impossible. After warming to 195 K the spectrum changed to a mixture of singlet at $g = 2.0006$ and the septet with the line shapes characteristic for H_α splitting of the $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{COO}^-$ radical and the total spectrum intensity decreased by 9%. Warming of the sample to 240 K decreased the spectrum intensity to 5% only. The resulting spectrum contained an isotropic septet of sharp lines with $a = 2.15$ mT belonging obviously to $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$ radical in addition to the spectrum of unknown species observed also in γ -irradiated *n*-butyric acid under similar conditions^{3,5}. The analogous isomerization of $\text{CH}_3\cdot\dot{\text{C}}\text{HCH}(\text{NH}_3)^+\text{COO}^-$ to $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$ has been observed earlier after warming of γ -irradiated α -aminobutyric acid to 100°C (ref.¹⁵).

When the irradiated sample was thermally annealed at 108 K the intensity of the doublet of radical anion decreased, while that of the singlet at $g = 2.0006$ corresponding probably to an acyl radical¹⁸ increased; the total spectrum intensity decreased by 10% only. After warming to 130 K the doublet completely disappeared and the remaining spectrum consisted of the singlet and spectra of alkyl radicals among which the septet of $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{COO}^-$ radical as the main component was identified; the total spectrum intensity decreased to 87%. During further warming all radicals decayed and after 240 K the same spectrum as obtained in the photo-lyzed and warmed sample was observed with the same intensity.

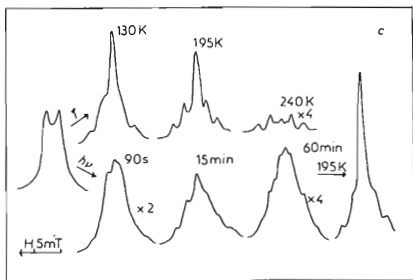


FIG. 3

Integrated ESR spectra of ammonium butyrate (c) after γ -irradiation at 77 K and thermal annealing (T) or optical bleaching ($h\nu$)

Ammonium isobutyrate. The spectrum of the sample irradiated at 77 K (Fig. 4) was composed of a singlet representing the main component, an octet and the small contribution of a septet ($a = 2.15$ mT). The 3 min photolysis caused the disappearan-

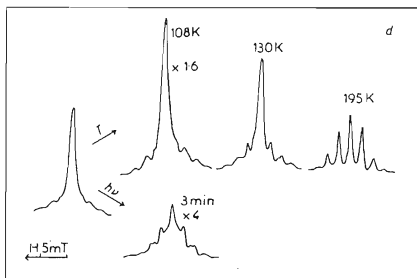


FIG. 4

Integrated ESR spectra of ammonium isobutyrate (*d*) after γ -irradiation at 77 K and thermal annealing (*T*) or optical bleaching ($h\nu$)

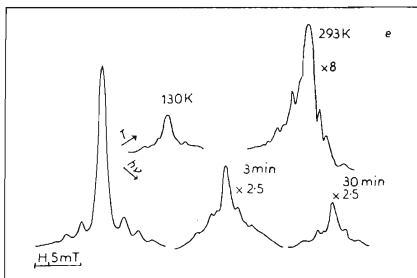


FIG. 5

Integrated ESR spectra of ammonium pivalate (*e*) after γ -irradiation at 77 K and thermal annealing (*T*) or optical bleaching ($h\nu$)

ce of the singlet and some increase of the septet spectrum in comparison with octet intensity; the total spectrum intensity decreased to 20%. The singlet with $g = 2.0023$ corresponds most likely to radical anion, the octet with the outer band shape characteristic of H_x splitting to $(CH_3)_2\dot{C}H$ and the isotropic septet is due to the $(CH_3)_2\dot{C}COO^-$ radical.

After warming of the irradiated sample to 108 K the total spectrum intensity decreased to 90% without occurring any observable change in relative amounts of radicals. At 130 K both, the singlet and the octet intensities, decreased and the septet intensity increased; the total spectrum intensity amounted to 85% of the original value. After warming to 195 K only the septet of $(CH_3)_2\dot{C}COO^-$ radical was observed with the intensity of 50% of the original value. The subsequent sample photolysis at 77 K brought about further decrease of radical concentration but only a small amount of $(CH_3)_2\dot{C}H$ (a few percent of the total intensity) appeared; this amount did not increase even after prolonged photolysis. These results show that the large decrease of the ESR spectrum intensity obtained after photolysis of the sample γ -irradiated at 77 K can be accounted for the simultaneous photobleaching of all radicals present.

Ammonium pivalate. The ESR spectrum recorded after the γ -irradiation at 77 K (Fig. 5) consisted of a singlet at $g = 2.0024$, the isotropic decet and the contribution from the isotropic spectrum with an odd line number. Similarly to pivalic acid⁵ the singlet belongs probably to the radical anion, the decet to the $(CH_3)_3\dot{C}$ radical and the odd line number spectrum is perhaps the septet of $(CH_3)_2\dot{C}COO^-$ radical. The intensities of both, the singlet and the decet, decreased rapidly on sample photolysis. Thus, the septet spectrum the intensity of which decreased more slowly could be reliably identified — its spectrum was quite distinct after 30 min photolysis. Upon thermal annealing at 130 K the singlet intensity diminished and a much weaker asymmetric singlet at $g = 2.0006$ appeared; also the septet spectrum became well observable. Between 130 and 200 K no spectral changes occurred. After warming to room temperature the septet intensity exceeded the decet intensity and the singlet of the acyl radical diminished.

Because of the photolytical instability of all radicals formed in ammonium pivalate the rough estimate of the radical anion amount could be made only by subtracting the theoretical spectrum of $(CH_3)_3\dot{C}$ radical from the overall spectrum. It showed that about one half of all radicals obtained at 77 K was due to the radical anion, similarly as in pivalic acid⁵.

CONCLUSIONS

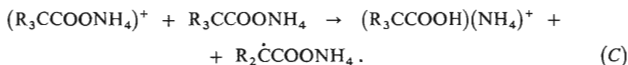
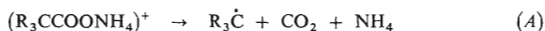
The ESR spectra of γ -irradiated ammonium propionate, n-butyrate and pivalate show that all radiolytic intermediates are very similar to those formed in the cor-

responding acids⁵. In ammonium isobutyrate the composition of radicals is also similar to that observed in isobutyric acid, but the ESR spectrum of the radical anion consists of the broad singlet while in isobutyric acid it is the doublet ($a = 2.3$ mT). This difference can be accounted for various spatial orientations of the unpaired electron orbital with respect to the C—H bond of α -carbon atom in ammonium salt and in acid. In the ESR spectrum of the ammonium acetate radical anion the rotating CH_3 group is responsible for the quartet hyperfine structure and the coupling to the distant matrix protons $a_{\text{max}} = 0.8$ mT (ref.¹⁰) brings about the unusual width of lines. In the matrix of acetic acid the rotation of CH_3 group of the radical anion is frozen in such a position to give the large interaction with one H_β atom ($a = 3.3$ mT) (ref.⁵).

The amounts of paramagnetic reduction products of γ -irradiation in most cases range 50% of all paramagnetic products as in the corresponding acids⁵. However, the presence of large amount (75%) of photobleaching radicals in γ -irradiated ammonium acetate at 77 K, ascribed to the radical anion, remains to be explained.

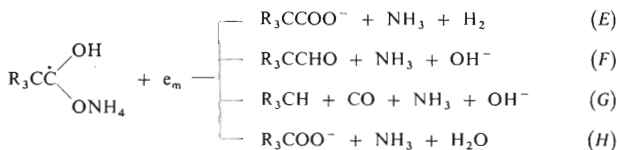
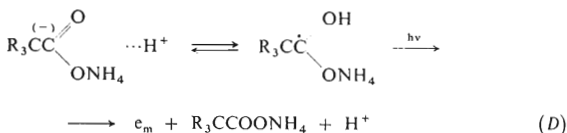
The discussion of mechanisms of formation of paramagnetic products of radiolysis and their photo- and thermal annealing is practically the same as in the analogous study concerning the acids⁵ when considering that the NH_4^+ group can dissociate to ammonia and a proton.

The radical anions are formed by trapping the electron evolved in the ionisation action of γ -rays. This reaction is probably followed by the stabilizing protonation. The alkyl radicals $\text{R}_3\dot{\text{C}}$ ($\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$) are probably the products of the radical cation decomposition according to equation (A). The secondary radicals $\text{R}_2\dot{\text{C}}\text{COONH}_4$ formed in minor amounts by γ -radiolysis at 77 K likely arise in the hydrogen abstraction from carboxylates by $\text{R}_3\dot{\text{C}}$ radicals according to equation (B) and/or by radical cations according to equation (C):

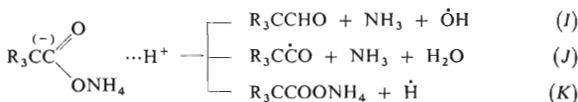


The photobleaching decay of radical anions can be explained by the mechanism suggested previously for carboxylic acids^{5,19,20}. The UV light releases the trapped electrons from the radical anions which are in equilibrium with their protonated form having the property of the neutral radical (equation (D)). The mobile electrons (e_m) are selectively captured by remaining protonized radical anions to afford the nonparamagnetic decomposition products, e.g., according to equations

(E)–(H):



The thermal annealing of radical anions lies in their decomposition yielding $\dot{\text{O}}\text{H}$ or $\text{R}_3\text{C}\dot{\text{C}}\text{O}$ radicals or H atoms according to equations (I)–(K). All these intermediates are able to abstract hydrogen atom from carboxylates to give relatively stable radicals $\text{R}_2\dot{\text{C}}\text{COONH}_4$ which are usually the ultimate paramagnetic products of the radiolytic decomposition of ammonium carboxylates.



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