

ELECTRON SPIN RESONANCE SPECTRA OF ALIPHATIC FLUORO- ALKYL RADICALS IN POLYCRYSTALLINE STATE. II.*

GAMMA RADIOLYSIS OF TRIFLUOROACETIC ACID

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An aqueous solution of CF_3COOH and its sodium salt, irradiated by γ -radiation at 77 K, give ESR spectra of the $\dot{\text{C}}\text{F}_3$ radical the edge peaks of which are separated by 756 G. This value corresponds to the maximum principal value of the tensor of the F_α -interaction $A_{\text{max}}^{F_\alpha} = 253$ G. The pure acid CF_3COOH , after γ -irradiation at 77 K, gives a somewhat narrower spectrum (maximum 743 G). This indicates that the $\dot{\text{C}}\text{F}_3$ radical formed by γ -irradiation has valence angles that differ from those of the same radical obtained by a long stay at 77 K or by heating the irradiated sample of the acid to -160°C , which has the maximum width of the spectrum of 772 G. In both cases at the edges of spectra there are groups of bands of the width of 44 G indicating that the radical is fixed in several magnetically non-equivalent positions in the crystal lattice. The narrower spectrum cannot be interpreted as the spectrum of the radical-anion $\text{CF}_3\dot{\text{C}}\text{OOH}^-$ because the F_β atoms cannot achieve the value (the mean value) of $A_{\text{max}}^{F_\beta} = 248-218$ G at the same time. In both the acid and its sodium salt the $\dot{\text{C}}\text{F}_3$ radicals vanish by heating giving rise to the radicals $\dot{\text{C}}\text{F}_2\text{COOH}$ and $\dot{\text{C}}\text{F}_2\text{COO}^-$, respectively. In the aqueous solution of the acid they vanish completely without any trace. The temperature dependence of the F_α splitting of the latter radicals depends on the strength of the crystal lattice. The mechanism of the radiolysis of CF_3COOH is discussed assuming the abundance of the $\dot{\text{C}}\text{F}_3$ and $\dot{\text{C}}\text{F}_2\text{COOH}$ radicals that are supposed to be the products of the decomposition of the ionized species.

The products of the γ -radiolysis of the higher perfluoroacids, irradiated at 77 K, and the products of the subsequent reactions of primary radicals during the heating have been studied by their ESR spectra in the preceding paper¹. The observable paramagnetic species were radicals of the general formulae $\text{R}\dot{\text{C}}\text{F}_2$ and $\text{R}\dot{\text{C}}\text{FR}'$ ($\text{R} = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_6\text{F}_{13}, \text{CF}_2\text{COOH}$ or $\text{CF}_2\text{CF}_2\text{COOH}$ and $\text{R}' = \text{COOH}$ or COONa). Their identification is based on the observation that the total spectral width of the polycrystalline sample is given by the maximum splitting of F_α nuclei in the radical. The $\text{R}\dot{\text{C}}\text{F}_2$ radicals are the primary products stable at 77 K that are formed by the interaction of γ -radiation with the aqueous solutions of acids. In pure acids the $\text{R}\dot{\text{C}}\text{F}_2$ radicals have been found in an amount that is comparable with the amount of $\text{R}\dot{\text{C}}\text{FR}'$ radicals while in their sodium salts the amount of these radicals has been much lower than the amount of the $\text{R}\dot{\text{C}}\text{FR}'$ radicals. In the γ -irradiation of the trifluoroacetic acid at 77 K either the formation of the radical-anion or the formation of the radicals $\dot{\text{C}}\text{F}_3$ and $\dot{\text{C}}\text{F}_2\text{COOH}$ has been expected. Brown and Stiles² studied the radiolysis of the trifluoroacetic acid at 77 K but they recorded only the central part

* Part I: This Journal 37, 663 (1972). For notation, cf. Part I.

of the ESR spectrum and their interpretation of the spectrum of the secondary radical, formed by heating the sample to -80°C , has not been correct in spite of the correct assumption that it is due to the $\dot{\text{C}}\text{F}_2\text{COOH}$ radical. Rogers and Kispert³ have found the $\dot{\text{C}}\text{F}_3$ radical in the radiolysed single crystal of trifluoroacetamide at 77 K and they determined the principal values of the tensor of the hyperfine interaction of its F_α nuclei. By heating the crystal to the room temperature they obtained the spectrum of the $\dot{\text{C}}\text{F}_2\text{CONH}_2$ radical that has been measured also by other authors^{4,5}. After the irradiation of the ammonium trifluoroacetate at 77 K Srygley and Gordy⁶ have found a radical with three weakly non-equivalent atoms of fluorine, the hyperfine interaction tensors of which are very close to the tensors of F_α atoms of the $\dot{\text{C}}\text{F}_3$ radical³. They have concluded that it is a spectrum of a radical-anion with the unpaired electron on the carboxyl carbon. The ESR spectrum of the $\dot{\text{C}}\text{F}_3$ radical fixed in the polycrystalline matrix of an inert gas has been recently obtained⁷ in the photolysis of CF_3J at 4.2 K. The spectrum, in spite of its complexity, has been interpreted using the known tensor of the hyperfine interaction of fluorine in the $\dot{\text{C}}\text{F}_3$ radical³ and the more complete interpretation of the spectrum has been done by Maruani and coworkers^{8,9} by comparing the calculated theoretical spectrum with the experimental one. By heating to 35 K the formerly anisotropic spectrum of the fixed radical changed to the isotropic spectrum of the freely moving radical, the parameters of which were identical with those of the spectrum of $\dot{\text{C}}\text{F}_3$ radical obtained in the liquid phase by Fessenden and Schuler¹⁰. Iwasaki and coworkers¹¹⁻¹³ studied the radiolysis of polycrystalline sodium salts and amides of the mono-, di- and trifluoroacetic acids at the room temperature. From the total width of the spectrum, giving the number of F_α nuclei, and from the splitting of wings of spectra caused by H_α nuclei they have found that the derivatives of the monofluoroacetic acid gave rise to the $\dot{\text{C}}\text{FHCOO}^-$ and $\dot{\text{C}}\text{FHCONH}_2$ radicals, respectively, the derivatives of the difluoroacetic acid formed $\dot{\text{C}}\text{F}_2\text{COO}^-$, $\dot{\text{C}}\text{F}_2\text{CONH}_2$ and the corresponding amido radicals, respectively, and the derivatives of the trifluoroacetic acid gave $\dot{\text{C}}\text{F}_2\text{COO}^-$ and $\dot{\text{C}}\text{F}_2\text{CONH}_2$, respectively.

In this paper the γ -radiolysis at 77 K of the trifluoroacetic acid, of its aqueous solutions and of its sodium salt have been studied. After the irradiation the samples were gradually heated and the ESR spectra were measured at 77 K as well as at the temperature to which the sample was heated.

EXPERIMENTAL

The trifluoroacetic acid was supplied by Koch and Light Laboratories Co. The sodium trifluoroacetate was prepared by a controlled neutralization in an aqueous solution and by a subsequent evaporation of the solution. After pulverization it was dried in vacuum at 100°C and sealed at 10^{-5} Torr into a "spectrosil" tube of extrapure quartz. The approximately 6M aqueous solutions of trifluoroacetic acids formed solid glasses if cooled to 77 K. The samples of the acid and its aqueous solutions were degassed in "spectrosil" probes at 10^{-5} Torr and sealed. The samples were irradiated by a ^{60}Co source with a dose rate of $5 \cdot 10^{17}$ and $9 \cdot 10^{17}$ eV/ml/min for about 8–10 hours. The ESR spectra were measured in the X-band partly with the Decca Radar X-2 spectrometer using the 100 kc modulation and equipped with the 7 in. electromagnet of Newport Instruments and with the proton magnetomer for the calibration of the magnetic field, and partly with the JES-3B ESR spectrometer of J.O.E.L. Co., Tokyo. The samples were measured either at 77 K, immersed in the liquid nitrogen in a Dewar vessel in the cavity of the spectrometer or at temperatures reached in a variable temperature unit placed in the cavity. The external warming of samples was carried out by dipping the sample tubes in baths prepared by cooling organic solvents to their melting points.

RESULTS AND DISCUSSION

Samples of the trifluoroacetic acid, of its aqueous solution and of its sodium salt, after γ -irradiation at 77 K, gave the ESR spectra, the farthest very weak edges of which were always separated by more than 700 G. The total width of these spectra shows that it is the spectrum of the $\dot{\text{C}}\text{F}_3$ radical because it is roughly similar to the polycrystalline spectrum of the $\dot{\text{C}}\text{F}_3$ radical which was first measured by McDowell and coworkers⁷ and interpreted by Maruani and coworkers^{8,9}. In this paper the experimental spectra obtained in various matrixes are interpreted by comparing their parameters with those obtained by Rogers and Kispert³ for the $\dot{\text{C}}\text{F}_3$ radical in a single crystal of $\dot{\text{C}}\text{F}_2\text{CONH}_2$.

The $\dot{\text{C}}\text{F}_3$ Radical in the Aqueous Solution of CF_3COOH

While the spectrum of this radical in pure acid after the γ -irradiation at 77 K is very complicated, its aqueous solution gave under the same conditions a much simpler spectrum of the total width of 756 ± 2 G. In addition to the very weak edge singlets, the spectrum consisted of a strong asymmetric doublet in the center of the spectrum and of weaker asymmetric bands in regions separated by 200–350 G (Fig. 1A). However, the stronger bands, denoted by x, on the side of lower magnetic-field intensity do not belong to the $\dot{\text{C}}\text{F}_3$ radical but probably to an oxygen-containing radical. If the samples are heated from 77 K to -130°C no changes have been found in spectra measured at 77 K, but after heating to -100°C the whole spectrum disappeared.

The edges of the spectrum, recorded as the first derivative spectrum, similarly as in spectra of other fluoro radicals in the polycrystalline matrix^{1,2,7,10}, give signals resembling mutually antipode absorption bands. The distance between the tops of the antipode peaks is taken as the distance between the edges of absorption bands. This distance gives the maximum value of the total splitting in spite of the fact that the roughly constant amount of radicals giving the same splitting is achieved only at the edge of the derivative peak on its side towards the center of the spectrum¹. However, the derivative peaks in the edges of the spectra are actually very broad (with the band width at the half height of ~ 20 G) and it is therefore reasonable to assume that the maximum splitting, found in single crystals, would correspond to the distance between the tops of the derivative peaks. The peak tops can be determined rather precisely and with good reproducibility.

For the qualitative interpretation of the spectrum of the $\dot{\text{C}}\text{F}_3$ radical we can start with the knowledge of the tensor of the hyperfine interaction of F_α atoms in $\dot{\text{C}}\text{F}_3$ radical and with the fact that significant changes in the intensity of polycrystalline spectra of fluoro radicals appear in positions for which the tensor of the hyperfine interaction reaches $A_{\text{max}}^{\text{F}_\alpha}$ and $A_{\text{min}}^{\text{F}_\alpha}$, respectively. The tensors of the hyperfine interaction of fluorine in the $\dot{\text{C}}\text{F}_3$ radical from CF_3CONH_2 are nearly axially symmetrical with $A_{zz}^{\text{F}_\alpha} = 253$ G,

$A_{xx}^{F\alpha} = 92$ G and $A_{yy}^{F\alpha} = 88$ G, respectively³. The $\dot{C}F_3$ radical is somewhat non-planar (the angle of the C—F bond with the plane perpendicular to the direction of the $2p_z$ orbital of the unpaired electron is 17.8°) so that the direction of the longest axis of the tensor of F_α interaction need not coincide with the direction of the $2p_z$ orbital⁸. However, the maximum value of the tensor of the hyperfine interaction, attainable simultaneously for all three fluorine atoms, can be achieved only if the radical is oriented in such a direction that the $2p_z$ orbital of the unpaired electron is

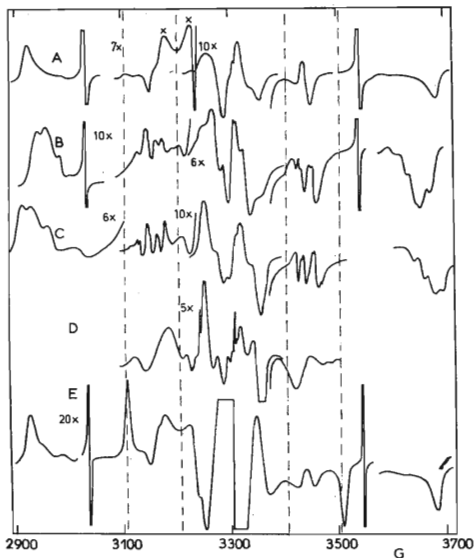


FIG. 1

ESR Spectra of the Trifluoroacetic Acid and Its Sodium Salt Irradiated by γ -Radiation at 77 K.

A 6M aqueous solution of CF_3COOH without heating, measured at 77 K (x — bands of the oxygen-containing radical); B anhydrous CF_3COOH without heating, measured at 77 K; C the same sample, after heating to $-140^\circ C$, measured at 77 K; D the same sample, measured at $-140^\circ C$; E CF_3COONa without heating, measured at 77 K. The numbers in the spectra indicate how many times the signal of the outer part of the spectrum has been amplified relatively to the central part of the spectrum. The regions separated by 200—350 G (cf. the text) are denoted by a dashed line. The strong doublet separated by 502 G in A, B and E is caused by hydrogen atoms trapped in the quartz of the sample tubes.

parallel to the direction of the magnetic field. On the other hand, a rotation of the radical around an axis parallel with the axis of the C_3 symmetry, equal to the direction of the $2p_z$ orbital (perpendicular to H), gives the minimum value of tensors of all three fluorine atoms under the assumption that $A_{xx}^{F\alpha} = A_{yy}^{F\alpha}$. Therefore in the polycrystalline sample only the radicals with $2p_z$ orbitals oriented along the magnetic field give a spectrum with maximum attainable splitting whereas the spectrum with minimum total splitting is due to radicals oriented so that the direction of their $2p_z$ orbitals is perpendicular to the magnetic field. The intensity of bands corresponding to the spectrum with minimum total splitting must be therefore higher than the intensity of bands with maximum splitting and it must be proportional to the abundance of the corresponding radical orientations. In both these cases the three fluorine atoms in the radical are completely, or nearly completely, equivalent and the radical spectrum for these orientations consists of 6 lines with intensity ratio 1 : 1 : 2 : 1 : 2 : 1. The splitting of the inner bands of the quartet 1 : 3 : 3 : 1, corresponding to the transitions with $M_1 = \pm 1/2$, is caused by an observable second-order effect. This splitting of the inner bands of the quartet amounts from 5 G for $2p_z \parallel H$ to 18 G for $2p_z \perp H$ (cf.³). The absorption spectrum of the $\dot{C}F_3$ radicals, emphasizing for illustration the higher intensity of the spectrum with minimum total splitting, is schematically plotted in Fig. 2. The doublet splitting of the strong central doublet of the transition $M_1 = \pm 1/2$, caused by the second-order splitting, is given by dotted lines. The asymmetry of bands corresponding to the transitions $M_1 = \pm 3/2_{\min}$

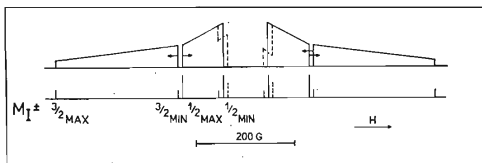


FIG. 2

The Expected Absorption Spectrum of the $\dot{C}F_3$ Radical in the Polycrystalline Matrix

The single crystal derivative ESR spectra for $A_{\max}^{F\alpha} = 253$ G and $A_{\min}^{F\alpha} = 90$ G (cf.³, the average value of $A_{yy}^{F\alpha} = 88$ G and $A_{xx}^{F\alpha} = 92$ G has been adopted) are schematically shown in the lower part. The second-order splitting of the transitions $\pm 1/2$ is given by the dashed line only for $A_{\min}^{F\alpha}$ (~ 18 G) because for $A_{\max}^{F\alpha}$ it amounts only to ~ 5 G (cf.³). The absorption spectrum of the $\dot{C}F_3$ radical in the polycrystalline matrix is schematically given in the upper part. The doublet structure in the center of the spectrum caused by the second-order splitting is drawn by a dashed line. The asymmetry of the experimental spectrum in the region of transitions $\pm 3/2_{\min}$ and $\pm 1/2_{\max}$ (regions separated by 200–350 G) is caused (except of a small second-order splitting of bands $\pm 1/2_{\max}$ (~ 5 G)) by the anisotropy of the g -factor, which shifts the mentioned bands in the direction denoted by arrows ($g_{zz} = 2.0024$, $g_{xx} = 2.0046$, $g_{yy} = 2.0038$, ref.³).

and $1/2_{\max}$, that appear in the ESR spectra of $\dot{C}F_3$ radicals in regions separated by 200–350 G (Fig. 1), is caused by the anisotropy of the g -factor of the radical (denoted by arrows) and in much lower extent by the second-order splitting of the transition with $M_1 = \pm 1/2_{\max}$ (not given).

The discussion, together with Fig. 2, shows clearly the origin of the strong signals in the polycrystalline ESR spectrum of the $\dot{C}F_3$ radical. Maruani and coworkers^{8,9} presented a detail interpretation of the polycrystalline spectrum of the $\dot{C}F_3$ radical in an inert matrix and they compared it with the theoretically calculated spectrum. The spectrum of the $\dot{C}F_3$ radical formed by the photolysis of CF_3J in the matrix of an inert gas at low temperatures is in overall features (the maximum width) identical with the spectrum of the $\dot{C}F_3$ radical in the matrix of the aqueous solution of CF_3COOH (Fig. 1A). However, it is more complicated and it strongly depends on the temperature of measurements and on the concentration of CF_3J in the inert gas⁸. The spectrum of the radical in the aqueous solution of the acid differs from the spectra of the radical in the inert gas and also from the calculated spectra, first of all by the higher intensity of the doublet in the center of the spectrum as compared with signals in the regions separated by 200 to 350 G and also by the larger width of all bands. However, the shape of bands in the whole spectral range and the maximum width of the spectrum agree with the spectrum calculated by Maruani and coworkers⁸.

The $\dot{C}F_3$ Radical in Pure Trifluoroacetic Acid

The trifluoroacetic acid irradiated by γ -radiation at 77 K gave an ESR spectrum that generally resembles the spectrum of the $\dot{C}F_3$ radical that was obtained in its aqueous solution, but in details the two spectra differ (Fig. 1B). The central doublet is distinctly split ($a_1 = 40$ G, $a_2 = 16$ G), the asymmetric bands separated by 200 to 350 G are in the acid split into asymmetric groups of bands and also the edge signals are split into several bands. However, the most distant bands of the spectrum are separated by only 743 G which corresponds to $A_{\max}^{F_x} = 248$ G.

This spectrum transforms slowly at 77 K and rapidly at -160° to $-140^\circ C$ into the spectrum given in Fig. 1C. The center of the spectrum is changed most markedly: there appears a doublet of doublets with splitting of 68 and 22 G, respectively, and also the shape of bands in regions separated by 200–350 G is changed. The total maximum width of the spectrum increases to 772 G, which corresponds to $A_{\max}^{F_x} = 257$ G. However, the innermost bands in the groups of edge signals are separated only by 684 G, *i.e.* $A_{\max}^{F_x} = 228$ G.

The more complicated structure observed in all parts of the spectrum of the anhydrous acid, if compared with the spectrum of its aqueous solution, and several values of $A_{\max}^{F_x}$ are not unexpected. In the single crystal of CF_3COONH_4 , irradiated by γ -radiation at 77 K, it has been found that the fluorine atoms of the $\dot{C}F_3$ radical are not completely equivalent. They give various values of $A_{\max}^{F_x} = 260, 257$ and 254 G, respectively, and, moreover, all the bands of the spectrum are split into doublets with 5–14 G. Srygley and Gordy⁶ assumed that the radical-anion with the unpaired electron on the carboxylic carbon is the paramagnetic species giving this spectrum and that the doublet splitting is caused by the hydrogen of the NH_4 group bound by a hydrogen bond to the oxygen of the carboxyl group.

While the splitting of α -hydrogen in radical-anions of aliphatic acids is not too different from the splitting of the β -hydrogen, in the perfluoro acids we should expect a rather high difference in the behaviour of α - and β -fluorine atoms. In Part I¹ it has been shown that the splitting of F_β atoms is maximum 94 G while $A_{\max}^{F_\alpha}$ at 77 K is always higher than 200 G. The main argument for the decision, whether the spectra observed after γ -irradiation of the pure trifluoroacetic acid are the spectra of the radical-anion or not, is the impossibility to achieve the same maximum interaction of 248–218 G for all three fluorine atoms for one orientation of the radical. It is more probable that the spectrum observed after γ -irradiation of CF_3COOH at 77 K corresponds to the radical $\dot{C}F_3$ which is firmly fixed in the matrix in unstable configurations that differ according to their localization in the crystal lattice. The lower values of $A_{\max}^{F_\alpha}$ and $A_{\min}^{F_\alpha}$, that are indicated by the smaller width of the spectrum and by the lower splitting of the central doublet in radicals that were not preheated, must be caused by a decrease of the electron density on fluorine atoms of the radical and by the corresponding change of valence angles. If heated to $-140^\circ C$ the $\dot{C}F_3$ radical achieves a more stable configuration but it is still firmly fixed in several different places of the crystal lattice so that the trapped radicals are magnetically non-equivalent.

Moreover, Rogers and Kispert³ proved that the $\dot{C}F_3$ radical trapped in CF_3CONH_2 occupies a different position than the CF_3 group in the molecule and that the $\dot{C}F_2CONH_2$ radical can change both its position and structure, depending on the temperature. Also in Part I¹ it has been

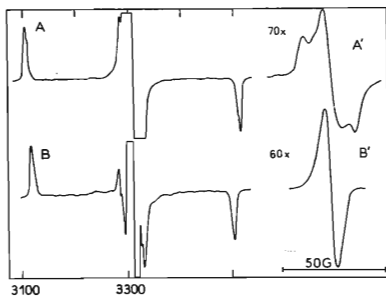


FIG. 3

ESR Spectra of CF_3COONa Irradiated by γ -Radiation at 77 K and Heated to $20^\circ C$

A CF_3COONa after heating to $20^\circ C$, measured at 77 K; B the same sample, measured at $20^\circ C$; A', B' — details in an expanded scale. Central parts of the spectra with the given attenuation and with the expanded magnetic-field scale are presented on the right hand side of the spectra. The center of the spectra is at 3308 G, practically at the same value as the signal of a free electron.

shown that the perfluoro radicals obtained by the radiolysis of perfluoro acids can change their configuration irreversibly or reversibly during the heating.

The measurement of the $\dot{\text{C}}\text{F}_3$ radical at -140°C (Fig. 1D) has shown that at this temperature the mobility of the radical increases reversibly. This is manifested by an overlapping of bands in regions separated by 200–350 G. The total width of the spectrum could not be measured due to the decrease of the intensity of the spectrum (because of the decreased difference in the population of both spin states at higher temperatures), or due to the large width of edge bands.

The $\dot{\text{C}}\text{F}_3$ Radical in Sodium Trifluoroacetate

The ESR spectrum of the $\dot{\text{C}}\text{F}_3$ radical in the sodium salt has been overlapped by a much more intense spectrum of the $\dot{\text{C}}\text{F}_2\text{COO}^-$ radical, especially in the central part of the spectrum (Fig. 1E). The observable parts of the $\dot{\text{C}}\text{F}_3$ spectrum in regions separated by 200–350 G are similar to the spectrum that has been obtained in the aqueous solution and also the edges of the spectrum show only simple bands separated by 756 G, which correspond to $A_{\text{max}}^{\text{F}_2} = 252$ G.

The $\dot{\text{C}}\text{F}_2\text{COOH}$ and $\dot{\text{C}}\text{F}_2\text{COO}^-$ Radicals

After heating to -130°C the ESR spectra of the $\dot{\text{C}}\text{F}_3$ radical are still observable in the aqueous solution of the acid, in pure acid and in its sodium salt, but after heating to -90°C they completely disappear. In the aqueous solution at temperatures higher than -90°C the signal vanishes completely, in pure CF_3COOH a new spectrum appears, consisting of a weak doublet separated by 406 G at 77 K and of a strong singlet in the center of the spectrum. In CF_3COONa after γ -irradiation the same spectrum has been found to be very strong already at 77 K and it was observed together with the spectrum of the $\dot{\text{C}}\text{F}_3$ radical, which, however, disappeared after heating to -90°C (Figs 1E and 3A). If measured at room temperature this spectrum became strictly symmetric (Fig. 3B). This spectrum was already observed in the polycrystalline CF_3COONa and in CF_3CONH_2 after γ -irradiation at the room temperature and by comparison with the spectra of single crystals it has been proved that it is caused by the $\dot{\text{C}}\text{F}_2\text{COO}$ and $\dot{\text{C}}\text{F}_2\text{CONH}_2$ radicals¹¹. The explanation of the shape of the spectrum is similar to that of the $\dot{\text{C}}\text{F}_3$ radical. The polycrystalline spectrum is a sum of all spectra for all the possible orientations of radicals relatively to the magnetic field. Because the radical $\dot{\text{C}}\text{F}_2\text{CONH}_2$ has two equivalent fluorine atoms at the room temperature and two nearly equivalent fluorine atoms³ at 77 K it can be expected that the $\dot{\text{C}}\text{F}_2\text{COOH}$ and $\dot{\text{C}}\text{F}_2\text{COO}^-$ radicals will behave in a similar manner. In this case the radicals in all their orientations will contribute by their triplets to the sum of the polycrystalline spectrum. The central triplet band corresponding to $M_1 = 0$ is common to all the radical orientations, regardless of the variation of the fluorine splitting from the maximum to the minimum value of the

tensor of the hyperfine interaction. The absorption spectrum measured at the room temperature should consist of a sharp, very strong band in the center of the ESR spectrum and of an absorption extending over the region between the values of minimum and maximum splitting of fluorine nuclei¹. Although in the actual derivative spectrum the central, very strong band is broadened at the room temperature, the weaker signals in the distance of 20 G from the center of the spectrum indicate the minimum value of the tensor of the hyperfine interaction of F_{α} of the axial symmetry (Fig. 3B). At 77 K the central band is substantially wider and asymmetric and the above-mentioned signals are poorly recognizable (Fig. 3A). With a higher resolution the fine structure of this central band is well observable. It is caused by the non-equivalent fluorine atoms³ (up to 20 G), by the anisotropy of the g -factor and by second-order effects (Fig. 3A, right).

Thermally Initiated Changes in the Spectra of $\dot{C}F_2COOH$ and $\dot{C}F_2COO^-$ Radicals

The $\dot{C}F_2CONH_2$ radical observed in the single crystal of CF_3CONH_2 has different values of the tensor of the hyperfine interaction $A_{max}^{F_{\alpha}}$ if measured at 77 K (202 G) or at the room temperature³ (180 G). The isotropic component of the tensor changes correspondingly from 77.3 G to 72.5 G and the maximum splitting of ^{13}C decreases from 147.5 G to 130 G. The value of the maximum splitting of ^{13}C at 300 K means that the radical is non-planar and that the C—F bonds contain an angle of 8° with the radical plane that is perpendicular to the $2p_z$ orbital of the unpaired electron. As indicated by higher value of a ^{13}C at 77 K the deviation from planarity increases at lower temperatures correspondingly to the greater s-character of the orbital of the unpaired electron³.

Even in the polycrystalline spectra of $\dot{C}F_2COOH$ and $\dot{C}F_2COO^-$ radicals in CF_3COOH and CF_3COONa it has been found that the total width of spectra, and consequently also the value of $A_{max}^{F_{\alpha}}$, decreases with the increasing temperature (Fig. 4). The temperature dependence of CF_3COOH has, however, a higher slope than that of CF_3COONa . Because both the splittings of F_{α} and ^{13}C depend similarly on the structure of the radical, it can be deduced from Fig. 4 that the $\dot{C}F_2COOH$, $\dot{C}F_2COO^-$ and $\dot{C}F_2CONH_2$ radicals are roughly equally non-planar at 77 K and that they become more planar with the increasing temperature. However, the $\dot{C}F_2COO^-$ radical needs much higher temperature for achievement of the same planarity than the $\dot{C}F_2COOH$ radical in the acid. An interesting effect has been observed during the heating of the γ -irradiated CF_3COONa to 100°C. If the ESR spectra were measured during the heating, a large amount of irregular signals appeared in the spectrum of $\dot{C}F_2COO^-$ between the edge and the center of the spectrum. When the same sample was measured at 77 K, the whole width of the spectrum was full of sharp irregular signals. A similar effect has been observed with CFH_2COOH , which, after γ -irradiation at 77 K, gave an unusually complicated spectrum and its structure changed during the heating even when the total width of the spectrum indicated that there was a radical with a single F_{α} atom. These effects can be explained by a par-

tial crystallization of samples so that larger portions of the samples have the same crystallographic orientation and the samples become inhomogeneous.

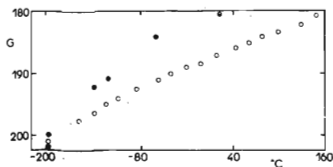


FIG. 4

The Dependence of $A_{\max}^{F_x}$ on the Temperature of the Measurement of the ESR Spectrum of Radicals

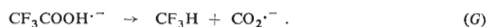
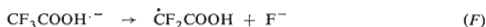
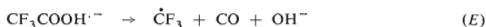
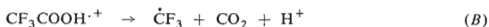
$\dot{C}F_2COOH$ (●), $\dot{C}F_2CONH_2$ (x) and $\dot{C}F_2COO^-$ (○) formed by the γ -radiolysis of $CF_3 \cdot COOH$, CF_3CONH_2 (cf.³) and CF_3COONa at 77 K.

Mechanism of Radiolysis of the Trifluoroacetic Acid

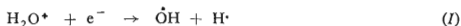
From the products of the radiolysis of aliphatic mono- and dicarboxylic acids it follows that the main process in the radiolysis of acids is their decarboxylation¹⁴⁻¹⁶. In the simplest case of the acetic acid, along with CO_2 , the gaseous products are CH_4 , C_2H_6 , H_2 and CO (cf.^{17,18}). While CH_4 and C_2H_6 are certainly formed by CH_3 radicals, the mechanism of the formation of H_2 and CO is not sufficiently explained. The final products of the radiolysis of perfluoroacids are not known but the paramagnetic intermediates — the $R\dot{C}F_2$ and $R\dot{C}FCOOH$ radicals — indicate¹ that the mechanism of the radiolysis is in both cases very similar. The trifluoroacetic acid and its aqueous solution after γ -irradiation at 77 K give only the $\dot{C}F_3$ radical. The process of the radiolytic decomposition of CF_3COOH is therefore much more specific than in higher perfluoroacids because there is not release of fluorine but exclusively the decarboxylation cleavage.

It can be assumed that the ionization of the trifluoroacetic acid by the γ -radiation gives rise to radical-anions and radical-cations (A). These two species were found¹⁹ in the γ -irradiated dicarboxylic acids at 4.2 K. The former was found^{20,21} also in the acetic acid and in higher aliphatic acids at 77 K. Radical-anions with an unpaired electron in the low-energy nonbonding orbital are evidently more stable than the paired radical-cations. It can be assumed that the radical-cations decompose rapidly according to Eq. (B) with the formation of $\dot{C}F_3$ and CO_2 . The reaction complementary to the decomposition of the radical-cation could be the reaction of the radical-anion with a proton according to Eq. (C) or a spontaneous decomposition of the radical-anion according to one of the equations (D)–(G):



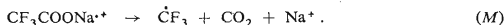


The decompositions of the radical-anion according to (C), (D), (E) cannot be followed by ESR using the described method because the H atoms recombine at temperatures lower than 77 K and the origin of $\dot{\text{C}}\text{F}_3$ radicals cannot be determined. However, it is sure that the radical-anion of the trifluoroacetic acid does not decompose with the formation of $\dot{\text{C}}\text{F}_2\text{COOH}$ according to Eq. (F). The decomposition of the radical-anion to $\text{COO}\cdot^-$ had been assumed in the irradiated succinic acid because a singlet signal has been detected which belongs with high probability to this species²². However, the mentioned signal of $\text{COO}\cdot^-$ has been observed only with very high energy of the microwave radiation when there appears the saturation effect in the aliphatic radicals. These experiments have not been done in the measurements of the ESR spectra of perfluoro radicals. With the usual energies of the microwave radiation no singlet that could be ascribed to $\text{COO}\cdot^-$ has been observed in the ESR spectra. In roughly 6M aqueous solutions of the trifluoroacetic acid no appreciable effect of water on the mechanism of decomposition at 77 K is expected, because Garisson and coworkers²³ found that in aqueous solutions of the acetic acid the yields of H_2 , H_2O_2 and $(\text{CH}_2\cdot\text{COOH})_2$ (which are the products of water radiolysis and of the interaction of OH radicals and H atoms with CH_3COOH) decrease very rapidly with the increasing concentration of the acid. In contrast to the acetic acid, in the trifluoroacetic acid no fluorine abstraction by an OH radical or by H atoms giving rise to $\dot{\text{C}}\text{F}_2\text{COOH}$ has been found. However, it is possible that the acid scavenged all electrons formed in the ionization of water according to Eq. (H) and prevented thus any formation of $\dot{\text{O}}\text{H}$ and $\text{H}\cdot$ radicals which are otherwise formed by the reaction (I):



The radical-anion formed in the reaction (K) does not decompose with the formation of $\dot{\text{C}}\text{F}_2\text{COOH}$ radicals (according to (F)) in spite of the fact that a similar decomposition with the formation of $\text{R}_2\dot{\text{C}}\text{COOH}$ and Cl^- has been observed in aqueous solutions of aliphatic chloro acids²⁴. On the other hand, in sodium salts F^- is formed according to Eq. (L) because even at 77 K the concentration of the $\dot{\text{C}}\text{F}_2$.

.COO⁻ radical is higher than the concentration of $\dot{\text{C}}\text{F}_3$ radicals formed by the decarboxylation decomposition (M):



In this case the decarboxylation reaction (M) must be slowed down by some competing reaction, if we do not want to take into consideration that a part of the $\dot{\text{C}}\text{F}_3$ radicals in the moment of their formation is capable to react with a fluorine atom of the neighbouring molecule giving rise to the $\dot{\text{C}}\text{F}_2\text{COO}^-$ radical.

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