

ELECTRON SPIN RESONANCE SPECTRA OF ALIPHATIC  
 FLUOROALKYL RADICALS IN POLYCRYSTALLINE STATE. I.  
 GAMMA RADIOLYSIS OF PERFLUORO ACIDS

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High number of fluoro radicals of the  $\dot{R}CF_2$  and  $\dot{R}CFR'$  types ( $R$  = fluoroalkyl,  $R'$  = carboxyl), formed by the  $\gamma$ -radiolysis of perfluoro acids, their aqueous solutions and sodium salts at 77 K and by subsequent heating, has been used to show that the method of radical identification, determining the number of  $F_\alpha$  atoms from the total width of the spectrum, is general and that the sufficient homogeneity of the polycrystalline samples is the only condition for its application. By the  $\gamma$ -irradiation of aqueous solutions of these acids at 77 K only  $\dot{R}CF_2$  radicals are formed, in pure acids the mixture of both  $\dot{R}CF_2$  and  $\dot{R}CFR'$  radicals is formed while in salts the radicals  $\dot{R}CFR'$  are formed predominantly. If heated, the radicals  $\dot{R}CF_2$  disappear and give rise to radicals  $\dot{R}CFR'$ . The structural variety appearing in wings of the spectra indicates that the wing structures, the separation of which determines  $A_{max}^{F_\alpha}$ ,\* reflect the interaction of  $F_\beta$  nuclei of the radicals as it would manifest itself in single crystal at its orientation in the magnetic field giving  $A_{max}^{F_\alpha}$ . A relatively frequent doublet structure in wings of the spectra with different separation of doublet peaks shows that one  $F_\beta$  atom causes zero splitting whereas the second  $F_\beta$  atom gives rise to splitting varying from values close to zero up to 94 G. Reversible and irreversible changes of both  $A_{max}^{F_\alpha}$  and  $a^{F_\beta}$  have been observed in  $\dot{R}CFR'$  radicals at various temperatures as a consequence of changes in planarity of radicals and in configuration of the  $F_\beta$  atoms with respect to unpaired electron orbital.

In spite of numerous electron spin resonance (ESR) studies on the mechanism of radiolysis of aliphatic acids, only few studies have been published on the radiolysis of their fluorinated analogues<sup>1</sup>. One of the reasons of this lower interest can be seen in the difficult interpretation of the ESR spectra of fluoro radicals in the polycrystalline state, though the main parameters of the hyperfine interaction of  $F_\alpha$  and  $F_\beta$  are well known from several ESR studies of single crystals of salts and amides of the simplest perfluoro acids<sup>2-6</sup>. The values of the isotropic interaction of the  $\alpha$ -fluorine have been obtained by ESR measurements of the radiolysis of fluorinated hydrocarbons in the liquid state at low temperatures or in matrixes of inert gases that permit rotation of trapped radicals<sup>7</sup>. Iwasaki and coworkers<sup>8</sup> studied the identification of fluoro radicals in polycrystalline substances and they found that the  $\dot{C}HF_2COO^-$ ,  $CF_3\dot{C}FCOO^-$  and  $CF_3CF_2\dot{C}FCOO^-$  radicals, formed by the radiolysis of sodium salts and amides of the respective acids at the room temperature, gave ESR spectra of the overall width exceeding 200 G. The

\* Notation used:  $A_{max}^{F_\alpha}$  the maximum principal value of the tensor of the hyperfine interaction of  $F_\alpha$ ;  $a^{F_\beta}$  splitting of  $F_\beta$ .



spectrum of the  $\dot{C}F_2COO^-$  radical was roughly twice wider. They assumed that the overall width of the spectrum of fluoro radicals reflected the maximum splitting of  $F_\alpha$  nuclei ( $\approx 200$  G). This value is in a good agreement with results obtained in studies of radicals in single crystals<sup>2-5</sup>. This method of the determination of the number of  $F_\alpha$  nuclei in radicals according to the overall width of the spectrum has been later used also for the identification of radicals in the  $\gamma$ -irradiated polytetrafluoroethylene at low temperatures<sup>10-12</sup>. It is assumed that the fine structure that appeared in the wings of spectra reflected the isotropic interaction of  $H_\alpha$  or  $F_\beta$  nuclei<sup>8-12</sup>.

In this paper the  $\gamma$ -radiolysis of fluoro acids, their aqueous solutions and sodium salts at 77 K has been investigated and ESR spectra of irradiated samples have been measured during a gradual heating up to temperatures at which the radicals vanish. The aim of this study is to verify the applicability of the method to the determination of  $F_\alpha$  atoms in radicals from the total spectral width of the polycrystalline samples and to obtain an idea on the anisotropic behaviour of  $F_\beta$  nuclei which is not sufficiently known from the studies on single crystals. The ESR spectra of polycrystalline samples are an important supplement to the studies of single crystals as they give information in advance on the splitting of all the participating nuclei, which will appear when  $A_{max}^{F_\alpha}$  is achieved. Moreover, they reflect the structural changes and the corresponding changes of splittings in the course of heating the samples and also indicate processes in which the sample crystallization occurs. The ESR spectra of polycrystalline samples of fluorinated compounds that crystallize but hardly in single crystals are an important source of information on the processes going on in their radiolysis and photolysis.

## EXPERIMENTAL

The pentafluoropropionic, heptafluorobutyric, pentadecafluorooctanoic, tetrafluorosuccinic and hexafluoroglutaric acids have been obtained from the Koch Light Laboratories Co. Ltd. Their sodium salts were prepared by the controlled neutralisation in aqueous solution and by successive crystallization from the concentrated solutions. The salts were dried by heating to 100°C in vacuum of  $10^{-4}$  Torr. Along with these compounds also the aqueous solutions of acids were  $\gamma$ -radiolyzed, containing 30–50 vol. % of water. The aqueous solutions if cooled rapidly to 77 K formed glasses while the pure acids gave polycrystalline solids. Evacuated samples ( $10^{-5}$  Torr) sealed in "Spectrosil" tubes of specially pure quartz have been radiolyzed in the liquid nitrogen bath until a sufficient intensity of radical signals was achieved in the far wings of the spectra. With the  $^{60}Co$ -source dose rate of about  $5 \cdot 10^{17}$  eV/ml/min the irradiation times were about 10 hours. The irradiated samples were measured on the Decca Radar X-2 spectrometer in which the 100 kHz modulation is used and which is equipped with the 7 in. electromagnet of Newport Instruments and by the proton magnetometer for the calibration of the magnetic field. The heating of samples to the desired temperature has been done by plunging the samples into liquids cooled to their freezing temperatures (solid-liquid mixtures) by liquid nitrogen. As a rule the samples were measured in liquid nitrogen but in a series of experiments they were heated directly in the cavity of the spectrometer and measured at the chosen temperature in the range from  $-170$  to  $+200^\circ C$ .

## RESULTS AND DISCUSSION

*The Method of Radical Identification and the Shape of Spectra*

From acids studied in this paper only the radicals with one or two fluorine atoms on the carbon atom with an unpaired electron ( $F_\alpha$  atoms) can be obtained, *i.e.* radicals  $R\dot{C}F_2$  or  $R\dot{C}FR'$ , respectively, where  $R = CF_3$ ,  $CF_3CF_2$ ,  $CF_3(CF_2)_4CF_2$ ,  $CF_2COOH$ ,  $CF_2CF_2COOH$  and  $R' = COOH$ ,  $COONa$  or  $COO^-$ , respectively. The  $\dot{C}F_3$  radical, the spectrum of which will be described in the subsequent paper<sup>13</sup>, has not been found in these samples.

The spectra of polycrystalline samples are a sum of all the spectra that would be observed in studies with single crystals comprising all the possible orientations of the radicals in the magnetic field. The tensor of the hyperfine interaction of  $F_\alpha$  is strongly anisotropic. It yields  $A_{\max}^{F_\alpha} = 200$  G and the other two principal values of the tensor are substantially lower and close to each other ( $\sim 20$  G). The absorption and derivative ESR spectra of the simplest radicals  $R\dot{C}FR'$  and  $R\dot{C}F_2$  (both R and R' have no atoms with a nuclear spin in beta position) with the principal tensor values of the

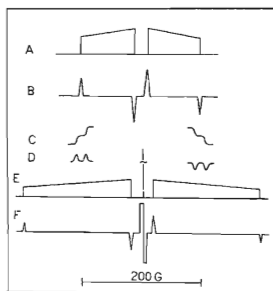


FIG. 1

The Schematic Shape of the Absorption and Derivative ESR Spectra as Expected for the Radicals  $R\dot{C}FR'$ ,  $R\dot{C}FH$ , and  $R\dot{C}F_2$ , Respectively (R, R' contain no atoms with a nuclear spin in an interaction with the unpaired electron)

In all radicals:  $A_{\max}^{F_\alpha} = 200$  G,  $A_{\min}^{F_\alpha} = 20$  G, there is an axial symmetry of the hyperfine interaction tensor. A the absorption (B the derivative) ESR spectrum of  $R\dot{C}FR'$  radical; C the edge of the absorption spectrum (D the edge of the derivative spectrum) of the  $R\dot{C}FH$  radical ( $a^H = 20$  G); E the absorption (F the derivative) ESR spectrum of the  $R\dot{C}F_2$  radical ( $a^{F1} = a^{F2}$  for all orientations of the radical in the magnetic field). The edges of the absorption spectra A and E should, actually, show a certain distribution curve and the corresponding derivative should then be continuous in all points, as it is shown in curves C and D.

anisotropic hyperfine interaction of the axial symmetry,  $A_{\parallel}^{F\alpha} = 200$  G and  $A_{\perp}^{F\alpha} = 20$  G, respectively, are schematically shown in Fig. 1 (A, B, E, F). Fig. 1 should explain the formation of the significant signals in the derivative spectra and it is constructed from the assumed absorption spectra using the knowledge of the principal values of the tensor of the hyperfine interaction. In the construction of spectra the second-order effects have been neglected, *i.e.* the appearance of transitions with  $M_1 \neq 0$ ,

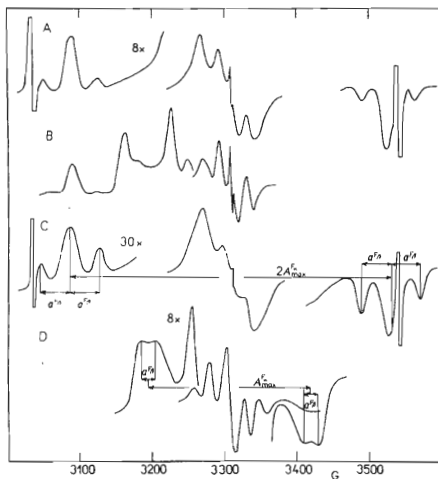


FIG. 2

Primary and Secondary Radicals in the Aqueous Solutions of the Perfluorosuccinic and Perfluoroglutaric Acids

A Perfluorosuccinic acid after  $\gamma$ -irradiation at 77 K (the radical  $\dot{C}F_2CF_2COOH$ ); B the same sample, the spectral wing after heating to  $-98^\circ C$ , the center of the spectrum after heating to  $-83^\circ C$ , both measured at 77 K (radicals  $HOCCF_2\dot{C}FCOOH$  and  $\dot{C}F_2CF_2COOH$ , respectively); C perfluoroglutaric acid after  $\gamma$ -irradiation at 77 K (radical  $\dot{C}F_2CF_2CF_2COOH$ ); D the same sample after heating to  $-98^\circ C$ , measured at 77 K (radical  $HOCCF_2CF_2\dot{C}FCOOH$ ). In the spectrum B the spectral wing at the higher magnetic field has not been measured but spectra of other samples of the same substance were symmetric under similar conditions. Sharp signals in the center of spectra at 3308 G are due to electrons trapped in quartz of the vessel. Numbers at spectral wings denote how many times the signal had to be increased when the spectral wings were recorded, in comparison with the record of the center of the spectrum. The strong doublet separated by 502 G is due to H atoms trapped in quartz of the vessel (it disappears after heating to  $-160^\circ C$ ).

influencing the central part of the polycrystalline spectrum<sup>9,14</sup> but not changing their outskirt parts. The exact shape of the absorption spectrum between the maximum and minimum of splitting of  $F_\alpha$  is not precisely known. The record of the derivative spectra shows that the first derivative is constant and close to zero when going from the value of the maximum splitting towards the center of the spectrum. Therefore the straight-line approximation with a low slope from the value of maximum splitting is correct up to certain distance from the value of minimum splitting. When the unpaired electron is also in an interaction with some other nuclei giving lower splitting, this splitting will appear distinctly only in the outskirts of the spectrum because in the center of the spectrum there is a strong overlap and spectrum becomes very complicated. The shapes of the shoulders of the absorption spectrum and wing peaks of derivative spectrum of the  $\dot{R}\dot{C}F_2R'$  radical (given in parts A and B of Fig. 1), which would be experimentally observed, are shown in parts C and D of Fig. 1. The group R of this radical contains a nucleus giving a splitting of 20 G for such an orientation of the radical when  $a^{F\alpha}$  is in maximum. From Fig. 1 it follows why the edges of derivative spectra look like composed of mutually antipode absorption bands. Moreover, from parts E and F of Fig. 1 it is evident that the central part of the spectrum, formed either by the central triplet band common for all the orientations of the radical or by the inner quartet bands at a weak non-equivalence of the  $F_\alpha$  atoms, is much stronger for the  $\dot{R}\dot{C}F_2$  radical than for the  $\dot{R}\dot{C}F_2R'$  radical.

The total spectral width is measured as the distance between the peak tops of the edge antipode signals which correspond to half the value of the absorption in the vicinity of the edge of the absorption spectrum. The maximum splitting values  $F_\alpha$  are then defined by the distance between the centers of structures observed in the both wings of spectrum, as far as these centers can be determined (Fig. 2C, D). Values thus obtained are in agreement with values obtained from the single crystal studies of  $CF_3\dot{C}FCONH_2$  radical<sup>5</sup> and  $\dot{C}F_2CONH_2$  radical<sup>2-4</sup>. The splitting values determined in this way do not depend on the shape of bands and are well defined. However, it is not clear whether it would not be more correct to measure the distance between the edges of peaks on their sides oriented towards the center of the spectrum but the large width of derivative peaks in wings of the polycrystalline spectrum indicates that the actual value of  $A_{\max}^{F\alpha}$  is shifted towards the vicinity of peak tops.

### *Radicals Obtained by $\gamma$ -Irradiation at 77 K and Their ESR Spectra*

At 77 K the ESR spectra of all samples had their central parts of the width of about 100 G roughly ten times stronger than the bands in the wings of spectra. The centers of the hyperfine structures of wing peaks were separated by  $444 \pm 12$  G corresponding to the maximum interaction of two  $F_\alpha$  nuclei with an unpaired electron so that the radical should have the general formula  $\dot{R}\dot{C}F_2$ . The value  $A_{\max}^{F\alpha} = 222 \pm 6$  G lies, as expected, between  $A_{\max}^{F\alpha} = 202$  and 253 G that were found for radicals  $\dot{C}F_2COO^-$

and  $\dot{C}F_2CONH_2$  (cf.<sup>3,4</sup>) and for the radical  $\dot{C}F_3$ , respectively<sup>4</sup>. Centers of spectra of all radicals (both  $R\dot{C}F_2$  and  $R\dot{C}FR'$ ) are found at the value of the magnetic field of 3308 G and the  $g$ -values of fluoro radicals do not differ from those found for alkyl radicals. The wings of spectra of  $R\dot{C}F_2$  radicals are described in Table I where also the temperature intervals of their existence are given.

Monocarboxylic acids give mostly a doublet structure in wings of spectra of  $R\dot{C}F_2$  radicals, but the doublet splitting varies, however, widely (from 7 to 66 G). In the perfluorosuccinic acid and in its sodium salt the wings in spectra of  $R\dot{C}F_2$  are composed only of broad singlets and these are mutually separated by 436 and 432 G, respectively (Fig. 3A, D). The radical giving this spectrum is evidently  $\dot{C}F_2CF_2COOH$  and not  $\dot{C}F_2COOH$  as this one produces relatively sharp singlets separated by 404 G at 77 K and by maximum 380 G at 30°C (ref.<sup>4,13</sup>). The  $\dot{C}F_2CF_2COOH$  radical had

TABLE I

Description of the ESR Spectra of Primary Radicals  $R\dot{C}F_2$  and Their Stability

Samples were  $\gamma$ -irradiated at 77 K and then gradually heated. ESR spectra were measured at 77 K.

Sample	$A_{\max}^{F_a}$ G	Structure of spectral wings	Decreases °C	Disappears °C	Amount of $R\dot{C}FR'$ at 77 K relatively to $R\dot{C}F_2$	
$C_2F_5COOH$	227	1 : 1, $a = 58$ G	-130	- 60	more	
$C_2F_5COOH + H_2O$ (66%)	}	not measured	-160	-130	0	
$C_2F_5COONa$		222	1 : 1, $a = 66$ G	-130	- 60	much more
$C_3F_7COOH$	228	1 : 1, $a = 24$ G	-130	- 60	comparable	
$C_3F_7COOH + H_2O$ (66%)	}	223	1 : 1 : 1 : 1, $a = 26$ G	-160	-130	0
$C_3F_7COONa$		220	1 : 1, $a = 22$ G	-130	- 90	much more
$C_7F_{15}COOH$	224	1 : 1, $a = 7$ G <sup>a</sup>	-130	0	negligible	
$C_7F_{15}COONa$		<sup>b</sup>	-130		much more	
$(CF_2COOH)_2$	218	broad singlet	- 83	over 100	less	
	212	<sup>c</sup> broad singlet				
$(CF_2COOH)_2 + H_2O$ (50%)	}	218	1 : 4 : 1, $a = 36$ G	-130	- 83	0
$(CF_2COONa)_2$		216	broad singlet	- 60	over 100	comparable
	203	<sup>c</sup> broad singlet				
$(CF_2)_3(COOH)_2$	222	1 : 2 : 1, $a = 38$ G	-130	- 83	0	
$(CF_2)_3(COOH)_2 + H_2O$ (50%)	}	222	1 : 2 : 1, $a = 38$ G	-160	-130	0

<sup>a</sup> After heating over  $-98^\circ C$  the doublet becomes a broad singlet; <sup>b</sup> present in an insignificant amount; <sup>c</sup> ESR spectrum measured at room temperature.

a total spectrum width of 424 G at the room temperature. However, in the aqueous solution of the perfluorosuccinic acid a spectrum has been found the wings of which consisted of triplets 1 : 4 : 1,  $a = 36$  G. The appearance of the triplet 1 : 4 : 1 can be explained as a superposition of the triplet spectrum 1 : 2 : 1 and the singlet caused by two  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  radicals differing by the orientation of the  $\text{F}_\beta$  atoms in respect to the orbital of the unpaired electron. The possibility of such an orientation of  $\text{F}_\beta$  atoms is indicated also by the spectrum of the  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  radicals of the perfluoroglutaric acid. The radical of the perfluoroglutaric acid should be formed by decarboxylation, similarly as in the perfluorosuccinic acid and other monocarboxylic acids, because the spectrum wings are composed of triplets 1 : 2 : 1,  $a = 38$  G, and they remain unchanged also in the aqueous solution. The rupture of the alkyl chain in another position would give rise to two different radicals, one of which should be  $\dot{\text{C}}\text{F}_2\text{COOH}$ , which, however, has a lower value of  $A_{\text{max}}^{\text{F}_\alpha}$ . The whole spectra of  $\dot{\text{C}}\text{F}_2\text{CF}_2\text{COOH}$  and  $\dot{\text{C}}\text{F}_2\text{CF}_2\text{CF}_2\text{COOH}$  radicals formed by  $\gamma$ -irradiation of aqueous solutions of the perfluorosuccinic and perfluoroglutaric acids at 77 K are presented in Fig. 2 (A and C). In samples of acids and salts the spectra of  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  radicals are accompanied by the spectra of  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  radicals. The appearance of bands in the spectral regions corresponding to the splitting of one  $\text{F}_\alpha$  is not caused by the spectra of  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  radicals because these radicals formed in aqueous solutions of acids do not exhibit any derivative bands in the region of the edges of the  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$ -radical spectra, *i.e.* in the neighbourhood of the magnetic-field values of  $3308 \pm 100$  G. The ESR spectra of aqueous solutions of acids at low temperatures do not reveal any traces of the presence of ion-radicals as well as of the products of water radiolysis, namely OH radicals, which would cause an asymmetry of the central parts of spectra.

ESR spectra of  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  radicals in acids and salts show that — at the orientation of radicals in the magnetic field giving  $A_{\text{max}}^{\text{F}_\alpha}$  — one of the  $\text{F}_\beta$  atoms gives practically zero splitting while the second one causes splitting ranging from 0 up to 66 G (Table I), depending on the structure of the radical. In aqueous solutions of dicarboxylic acids  $a_1^{\text{F}_\beta} = a_2^{\text{F}_\beta} = 36$  and 38 G, respectively, in the solution of the butyric acid  $a_1^{\text{F}_\beta} = 2a_2^{\text{F}_\beta} = 52$  G (Table I). The radical  $\text{CF}_3\dot{\text{C}}\text{F}_2$  in the perfluoropropionic acid and in its salt gives a doublet ( $a = 58$  and 66 G, respectively) of broad bands which means that  $a_1^{\text{F}_\beta} = 58$  G,  $a_2^{\text{F}_\beta} \leq 10$  G and  $a_3^{\text{F}_\beta} \leq 5$  G.

### Thermally Initiated Transformations of Radicals

The overwhelming portion of  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  radicals in acids disappears by heating to  $-130^\circ\text{C}$  and in their aqueous solutions they disappear already at  $-160^\circ\text{C}$ . In sodium salts they disappear at  $-90^\circ\text{C}$ . The only exception is the perfluorosuccinic acid and its sodium salt in which the evidently very strong crystal lattice causes that the  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  radicals are observable up to  $100^\circ\text{C}$ .

In aqueous solutions of acids the spectra of  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  radicals are, by heating to the respective temperature, undoubtedly substituted by the spectra of  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  radicals.

These radicals are in this case formed from the molecule merely by an abstraction of fluorine by the primary radical  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$ . Even in acids the overwhelming portion of  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  radicals is similarly formed at the temperature at which the radicals  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  vanish. The perfluorosuccinic acid is again an exception as part of the  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  radicals disappears and gives rise to  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  radicals but the other part is stable up to the temperature at which the radicals  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  disappear, too.

The radicals  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  observed in acids and their salts when irradiated at 77 K have always a different fine structure in the wings of spectra than the radicals  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  formed by heating of the irradiated samples. In experiments with  $\text{CF}_3\text{CF}_2\text{COOH}$  it has been found that 10 days after the irradiation at 77 K the structure of the wings of the spectra of  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  changed but neither a decrease of  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  nor an increase of  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  has been observed. Hence, these radicals must be formed in one of the primary steps of the radiolysis that are fast enough at 77 K. In the case of  $\text{CF}_3\text{CF}_2\text{COOH}$  the radical  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  formed at 77 K as well as the radical formed by heating must be identical, *i.e.* it must be the radical  $\text{CF}_3\dot{\text{C}}\text{FCOOH}$ . However, their structures given by their orientation in the matrix should differ. By heating the acid to the temperature at which the secondary  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  radicals are formed, both the radicals  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  formed at 77 K and the newly formed one are similarly oriented in the matrix and give thus the same spectrum.

### ESR Spectra of the $\dot{\text{R}}\dot{\text{C}}\text{FR}'$ Radicals

The  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  radicals are thus formed partly by a thermally initiated abstraction of fluorine from molecules by the  $\dot{\text{R}}\dot{\text{C}}\text{F}_2$  radical, partly directly by the radiolysis at 77 K. The wing structures of their ESR spectra are described in Table II together with the temperature range in which they are stable. The secondary  $\dot{\text{R}}\dot{\text{C}}\text{FR}'$  radicals have the value of  $A_{\text{max}}^{\text{F}\alpha}$  ranging from 200 to 252 G depending on the structure of the radical and on the temperature of the measurement (Table II). The structure of wing peaks varies rather widely and it depends on the heating of samples and on the temperature of the measurement. Radicals with two  $\text{F}_\beta$  atoms give usually a doublet structure of wings and the splitting of the doublets ranges from 22 to 94 G.

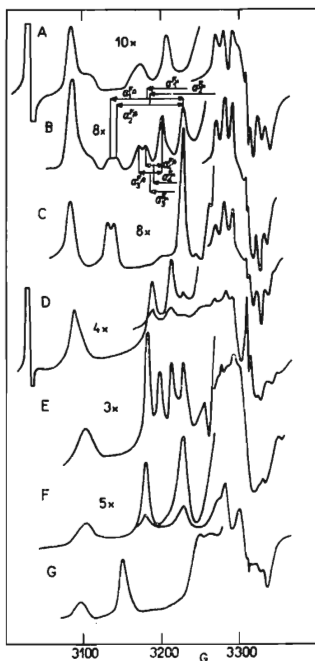
More complicated ESR spectra have been obtained with the perfluorosuccinic acid and its sodium salt. The complication is probably due to the formation of several chemically identical but magnetically non-equivalent radicals. In the polycrystalline perfluorosuccinic acid several secondary radicals  $\text{HOOC}\text{CF}_2\dot{\text{C}}\text{FCOOH}$  have been observed when heated to  $-130^\circ\text{C}$  that differ in their values of  $A_{\text{max}}^{\text{F}\alpha}$  and  $a^{\text{F}\beta}$ . Using the interpretation giving the minimum scattering of  $A_{\text{max}}^{\text{F}\alpha}$  in the sample heated to  $-130^\circ\text{C}$  up to  $-60^\circ\text{C}$  at least four radicals are present with the following parameters:  $a_1^{\text{F}\alpha} = 252$  G,  $a_1^{\text{F}\beta} = 92$  G,  $a_2^{\text{F}\alpha} = 242$  G,  $a_2^{\text{F}\beta} = 82$  G,  $a_3^{\text{F}\alpha} = 242$  G,  $a_3^{\text{F}\beta} = 30$  G,  $a_4^{\text{F}\alpha} = 232$  G,  $a_4^{\text{F}\beta} = 20$  G ( $a^{\text{F}\alpha} = A_{\text{max}}^{\text{F}\alpha}$ ). The splitting of the second  $\text{F}_\beta$  atom must be close to zero for each of these radicals (Fig. 3B). The radicals giving



lower values of  $a^{F\beta}$  disappear if heated to  $-30^\circ\text{C}$  and the intensity of the spectra of the remaining two radicals increases twice (Fig. 3C). If measured at 77 K this spectrum remains unchanged even if heated to  $100^\circ\text{C}$ . However, if measured at the room temperature it gives different values of  $a_1^{F\alpha} = 226$  G,  $a_1^{F\beta} = 70$  G,  $a_2^{F\alpha} = 238$  G,  $a_2^{F\beta} = 82$  G. The non-equivalence of the values of  $a^{F\alpha}$  ( $= A_{\text{max}}^{F\alpha}$ ) could be caused by the fact that the  $F_\alpha$  atoms of radicals localized in different positions of the crystallographic unit contain various angles with the radical's plane. A similar effect of temperature on the radical structure has been observed with  $(\text{CF}_2\text{COONa})_2$ . At the room temperature the values of splitting are different for both  $F_\beta$ ,  $a_1^{F\beta} = 29$  G,  $a_2^{F\beta} = 14$  G (Fig. 3E), but if heated to  $70^\circ\text{C}$  the radicals are reoriented so that at room temperature  $a_1^{F\beta} = 45$  G and  $a_2^{F\beta}$  approaches zero (Fig. 3F). However, if the same spectrum is measured at 77 K,  $a_1^{F\beta} = 94$  G,  $a_2^{F\beta} = 0$  (Fig. 3G).

FIG. 3  
The Transformation of Radicals of the Perfluoro-succinic Acid and Its Sodium Salt

A Perfluorosuccinic acid after  $\gamma$ -irradiation at 77 K; B the same sample after heating to  $-60^\circ\text{C}$ , measured at 77 K; C the same sample after heating to  $-30^\circ\text{C}$ , measured at 77 K; D sodium perfluoro-succinate after  $\gamma$ -irradiation at 77 K; E the same sample at  $20^\circ\text{C}$ ; F the same sample after heating to  $70^\circ\text{C}$ , measured at  $20^\circ\text{C}$ ; G the same sample as in F, measured at 77 K. As all the spectra are symmetrical, the spectral wings at higher field are not presented. In the spectrum G no center of the spectrum is given as it has been measured in another scale. Sharp signals in the centers of the spectra at 3308 G are due to electrons trapped in quartz of the vessel. Numbers at spectral wings denote how many times the signal has to be increased when recording the spectral wings in comparison with the centers of spectra.



The values of  $a^{F\beta}$  found for the sodium perfluorooctanoate (82 G), for the perfluorosuccinic acid (92 G) and for its sodium salt (94 G) are higher than the maximum values of the tensor of the hyperfine interaction  $A_{\max}^{F\beta} = 63$  and 71 G, respectively, found for the radical  $(\text{OCCF}_2\dot{\text{C}}\text{FCOO})^{2-}$  in  $\gamma$ -irradiated  $(\text{CF}_2\text{COONa})_2 \cdot 5 \text{H}_2\text{O}$  at the room temperature. However, the values of  $a^{F\beta}$  of the polycrystalline samples have been obtained at 77 K while at the room temperature much lower values have been always found. Unfortunately, an attempt to compare directly the values obtained for a single crystal of  $(\text{CF}_2\text{COONa})_2 \cdot 5 \text{H}_2\text{O}$  with the spectrum of a polycrystalline sample failed because the mentioned hydrate evidently does not bind water sufficiently strongly and in vacuum – when the polycrystalline sample was cooled down to 77 K – larger oriented regions have been formed and the sample became inhomogeneous.

### *Thermally Initiated Changes in the Structure of Radicals*

Because of the high anisotropy of  $a^{F\alpha}$  and  $a^{F\beta}$  the changes in the structure of radicals (*i.e.* the deviations of  $F_\beta$  nuclei in respect to the orbital of the unpaired electron) are easily observable in polycrystalline spectra of fluoro radicals. In the case of hydrocarbon radicals this is observed only rarely and by using single-crystal samples.

The reversible changes of  $A_{\max}^{F\alpha}$  and  $a^{F\beta}$  in measurements at various temperatures have been observed for all the  $\text{RCFR}'$  radicals. At 77 K always much higher values of  $A_{\max}^{F\alpha}$  and the higher splitting of  $F_\beta$  have been measured than at the room temperature (Table II).

The same effect in the behaviour of  $A_{\max}^{F\alpha}$  has been formerly observed by Rogers and Kispert<sup>4</sup> for the  $\dot{\text{C}}\text{F}_2\text{CONH}_2$  radical and it has been explained by the change of the radical planarity. In the subsequent paper<sup>13</sup> it has been shown that this change of the radical planarity is influenced by the magnitude of interaction of the radical with the matrix (it depends on the rigidity of the matrix).

The irreversible changes of spectra have been observed during the heating of all  $\text{RCFR}'$  radicals formed by the irradiation at 77 K. These changes indicate that the radicals (formed by  $\gamma$ -irradiation at 77 K) were trapped in a position with high energy and only the heating to a certain temperature allowed them to occupy a more stable position with lower energy, which has been manifested by another orientation of the  $\text{C}-\text{F}_\beta$  bonds in respect to the unpaired electron. These changes were best observable in the solid matrixes of the perfluorosuccinic acid and its sodium salt even in the region of highest temperatures (Table II, Fig. 3). In the perfluorosuccinic acid the radical  $\text{HOCCF}_2\dot{\text{C}}\text{FCOOH}$  has been found in several mutually irreversible configurations with various parameters  $A_{\max}^{F\alpha}$  and  $a^{F\beta}$ . These configurations appeared at 77 K and after heating to  $-130^\circ\text{C}$  or to  $-30^\circ\text{C}$ , respectively. In the sodium perfluorosuccinate the anion of the same radical appeared also in three mutually irreversible configurations: at 77 K, after heating to  $-130^\circ\text{C}$  and to  $70^\circ\text{C}$ , respectively.

TABLE II

Description of the ESR Spectra of Secondary Radicals  $\dot{R}CFR'$  ( $R' = COOH$  or  $COONa$ ) and the Temperature Interval of Their Existence

If not stated otherwise, the data in the Table relate to a sample heated to the temperature, at which the secondary radicals  $\dot{R}CFR'$  appear, and measured at 77 K. Radicals  $\dot{R}CFR'$  formed by heating that causes an abstraction of fluorine from molecules by the radicals  $\dot{R}CF_2$ , and the  $\dot{R}CFR'$  radicals formed by  $\gamma$ -irradiation at 77 K, after heating to the temperature of the formation of secondary radicals, have an identical ESR spectrum.

Sample	$A_{\max}^{F_x}$	Structure of spectral wings	Appears °C	Disappears °C
$C_2F_5COOH$	—	asymmetric (Fig. 4A)	-130	- 45
$C_2F_5COOH + H_2O$ (66%)	} 226	1 : >1 : >1 : 1, $a = 14-15$ G	-160	- 83
		217 at $-100^\circ C$ 1 : 3 : 3 : 1, $a = 14-15$ G		
$C_2F_5COONa$	220	asymmetric (Fig. 4D)	-130	+200
	214	at $-160^\circ C$ 1 : 3 : 3 : 1, $a = 18$ G		
	199	at $-90$ up to $+20^\circ C$ , $a = 18$ G		
$C_3F_7COOH$	224	1 : 1, $a = 50$ G	-130	- 45
$C_3F_7COOH + H_2O$ (66%)	} 218	too weak signal in spectral wings	-160	-130
$C_3F_7COONa$		201	6 bands with a center of symmetry at $0^\circ C$ , 1 : 1 : 1 : 1, $a_1 = 19$ , $a_2 = 35$ G	-130
$C_7F_{15}COOH$	226	1 : 1, $a = 22$ G, bands further split into triplets 1 : 2 : 1, $a = 7$ G	-130	+ 20
	212	at $+20^\circ C$ , 1 : 1, $a = 28$ G		
$C_7F_{15}COONa$	228	1 : 1, $a = 82$ G at $+20^\circ C$ , four bands separated by 30, 18 and 26 G	-130	+ 20
$(CF_2COOH)_2$	252-232	4 radicals with non-equivalent $A_{\max}^{F_x}$ (Figs 3B, C and the text)	-130	+100
$(CF_2COOH)_2 + H_2O$ (50%)	} 226	1 : 1, $a = 64$ G	-130	- 83
$(CF_2COONa)_2$		214	without heating, at 77 K, 1 : 1, $a = 24$ G	
	208	1 : 1 : 1 : 1, $a_1 = 29$ G, $a_2 = 14$ G	-130	+100
	206	after $70^\circ C$ , measured at $20^\circ C$ , 1 : 1, $a = 45$ G		
	218	the same, measured at 77 K, $a = 94$ G		
$(CF_2)_3(COOH)_2$	218	1 : 1, $a = 24$ G	-130	- 63
$(CF_2)_3(COOH)_2 + H_2O$ (50%)	} 218	1 : 1, $a = 24$ G	-130	- 83

### ESR Spectra of $\text{CF}_3\dot{\text{C}}\text{FCOOH}$ and $\text{CF}_3\dot{\text{C}}\text{FCOO}^-$ Radicals

The radicals  $\text{CF}_3\dot{\text{C}}\text{FR}'$  differ from other  $\text{R}\dot{\text{C}}\text{FR}'$  radicals by the behaviour of their  $\text{F}_\beta$  atoms because the  $\text{CF}_3$  group can freely rotate around the C—C bond. ESR spectra, indicating the mobility of the  $\text{CF}_3$  group, were studied for radicals formed in the samples of the acid, its aqueous solution (66 vol. %) and its sodium salt at various temperatures of the measurement.

The wings of ESR spectra of the  $\text{CF}_3\dot{\text{C}}\text{FCOOH}$  radical in the irradiated sample of the acid at 77 K, after heating to  $-130^\circ\text{C}$  up to  $-45^\circ$  are composed of several unequally strong and irregularly separated bands (Fig. 4A). On the other hand, the aqueous solution of the acid after heating to  $-160^\circ$  up to  $-100^\circ\text{C}$  gives at 77 K nearly equidistant quartets  $1 : > 1 : > 1 : 1$ , with  $a = 14-15\text{ G}$  separated by 226 G (Fig. 4B). When the same sample has been measured at  $-100^\circ\text{C}$ , the ratio intensities of quartet bands changed to  $1 : 3 : 3 : 1$  and at the same time the doublet in the center of the spectrum became split (Fig. 4C). A spectrum, practically identical with that one of Fig. 4C, has been obtained if the sample of the acid was measured at  $-60^\circ\text{C}$  (ref. <sup>1</sup>).

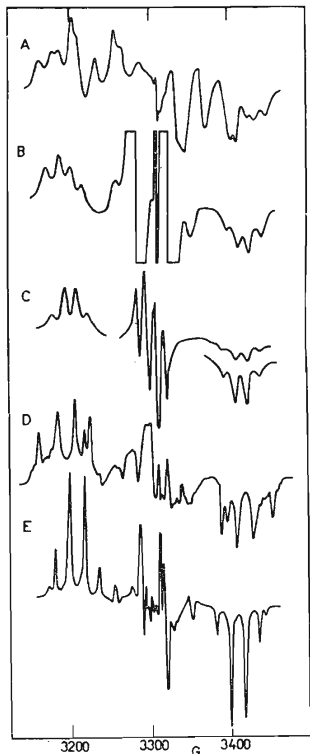


FIG. 4

Radicals  $\text{CF}_3\dot{\text{C}}\text{FCOOH}$  and  $\text{CF}_3\dot{\text{C}}\text{FCOO}^-$  in Polycrystalline Matrices

A  $\text{CF}_3\text{CF}_2\text{COOH}$  after heating to  $-60^\circ\text{C}$ , measured at 77 K; B  $\text{CF}_3\text{CF}_2\text{COOH}$  in  $\text{H}_2\text{O}$  (66 vol. %) after heating to  $-160^\circ\text{C}$ , measured at 77 K; C the same sample, measured at  $-100^\circ\text{C}$ ; D  $\text{CF}_3\text{CF}_2\text{COONa}$  after heating to  $20^\circ\text{C}$ , measured at 77 K; E the same sample, measured at  $20^\circ\text{C}$ ; all samples were  $\gamma$ -irradiated at 77 K.

For  $\text{CF}_3\text{CF}_2\text{COONa}$ , when measured at 77 K, the structure of spectral wings is internally asymmetric (Fig. 4D) and it does not change if previously heated to  $-130^\circ\text{C}$  up to  $+200^\circ\text{C}$ . However, if the same sample is measured at temperatures ranging from  $-170$  to  $+30^\circ\text{C}$  the wings of the spectra give a quartet of very sharp bands of intensities 1 : 3 : 3 : 1, separated by 18 G (Fig. 4E).

From these measurements it follows that the  $\text{CF}_3$ -group of the radical is fixed at 77 K, in pure acid, but in the aqueous solution at 77 K it performs a weakly hindered rotation and the entire radical is capable of reorienting movements as shown by the simple doublet center of the spectrum. At  $-100^\circ\text{C}$  in the solution and at  $-60^\circ\text{C}$  in the acid the rotation of the  $\text{CF}_3$ -group is practically unhindered as witnessed by the binomial ratio of intensities of the quartet and the splitting and narrowing of the doublet bands in the center of the spectrum indicates further loosening of the radical movements. In the sodium salt the radical  $\text{CF}_3\dot{\text{C}}\text{FCOO}^-$  is fixed even at high temperatures (*cf.* the complex center of the spectrum) but the  $\text{CF}_3$ -group of the radical, freely rotating at temperatures up to  $-170^\circ\text{C}$ , is at 77 K already strongly hindered. We can conclude that the radical as an entity is fixed best in the salt and most weakly in the aqueous solution of the acid, but the rotation of the  $\text{CF}_3$  group is in salt loosened at lower temperatures than in the acid and in its aqueous solution.

The parameters of the polycrystalline spectrum of the  $\text{CF}_3\dot{\text{C}}\text{FCOO}^-$  radical can be compared with data obtained by Lontz<sup>5</sup> for the  $\text{CF}_3\dot{\text{C}}\text{FCONH}_2$  radical in the single crystal of the amide at the room temperature. Lontz found that the maximum value of the tensor of the hyperfine interaction is  $A_{\text{max}}^{\text{F}_\alpha} = 201$  G and that the principal values of the tensor of the hyperfine interaction  $F_\beta$  of the freely rotating  $\text{CF}_3$  group are  $A_{1^\beta}^{\text{F}_\beta} = 36$  G,  $A_{2^\beta}^{\text{F}_\beta} = 17$  G and  $A_{3^\beta}^{\text{F}_\beta} = 14$  G, respectively. The splitting of the quartet bands was  $\sim 17$  G at the maximum value of  $A_{\text{max}}^{\text{F}_\alpha}$ . All these data are in good agreement with the results obtained from the polycrystalline spectrum of  $\text{CF}_3\text{CF}_2\text{COONa}$  (Table II). For single crystals cooled to 77 K Lontz obtained doublets of doublets instead of quartets, for orientations of the crystal, when no "site splitting" occurred. He assumed that the rotation of the  $\text{CF}_3$  group has been slowed down and that the  $F_\beta$  nuclei became magnetically non-equivalent. One of the three fluorine atoms gave the splitting of  $\sim 30$  G, the second one gave a doublet which could be just resolved and the third one caused only broadening of the observed bands. However, this explanation has been presented only for the orientation of the single crystal that did not give  $A_{\text{max}}^{\text{F}_\alpha}$ . Because the interaction of the  $F_\beta$  nucleus depends not only on the mutual orientation of the C— $F_\beta$  bond and the orbital of the unpaired electron but also on the orientation of the radical in the magnetic field<sup>5,6</sup>, it can be assumed that at the orientation of the radical giving  $A_{\text{max}}^{\text{F}_\alpha}$  the structure of wings in the polycrystalline spectrum would be found even in the spectrum of the single crystal. On the other hand, the observation, that the  $\text{CF}_3$  group with hindered rotation can give rise only to a doublet of broad bands, is in agreement with the observed polycrystalline spectrum of the  $\text{CF}_3\dot{\text{C}}\text{F}_2$  radical in the perfluoropropionic acid and in its sodium salt at 77 K (Table I).

### *Analysis of the Central Parts of Spectra*

The central parts of the ESR spectra of polycrystalline samples cannot be interpreted in detail as it already follows from the discussion to Fig. 1. In the  $\text{RCF}_2$  radicals

the intensity of the central parts of spectra is usually 10-times stronger in comparison with the wings of the spectrum (as judged by the heights of derivative peaks). The broad and strong center of the spectrum is formed mainly by the central band of the triplet (because  $a_1^{F\alpha} \approx a_2^{F\alpha}$ ) which is common for all or most of the orientations of the radical and its width is given mainly by the anisotropy of the splitting of  $F_\beta$  atoms. The central band of triplets is basically formed by a sum of all splittings of  $F_\beta$  atoms at all orientations of radicals in the magnetic field and, as it has been shown above, the splitting of  $F_\beta$  can reach up to 90 G. Examples of the spectra of  $\dot{R}CF_2$  radicals are presented on Fig. 2A and 2C. The centers of spectra of  $\dot{R}CF_2$  radicals of the propionic acid and its aqueous solution are similar to Fig. 2A. The center of the spectrum of the aqueous solution of the perfluorobutyric acid looks like the spectrum on Fig. 2C.

On the other hand, the  $\dot{R}CFR'$  radicals have the intensity of peaks in the central part of the spectrum only slightly higher or comparable with the intensity of edge peaks. At low temperatures the centers of spectra are usually complex and often asymmetric (with the exception of the spectra of aqueous solutions of several acids) but at higher temperatures of the measurement symmetric and sharp bands of higher intensity appear in the central parts of spectra of acids. For example, the  $CF_3\dot{C}FCOOH$  radical has an asymmetric weak center of the spectrum at 77 K in the acid, a very sharp quartet 1 : > 1 : > 1 : 1 (Fig. 3) in the acid at  $-60^\circ C$  and in the solution at  $-100^\circ C$ , respectively. Similarly, at  $-60^\circ C$  the broad singlets in the center of the spectrum of the perfluorobutyric acid change into triplets 1 : > 1 : 1 of splitting  $a = 16$  G. This is also the case of the spectrum of the perfluorooctanoic acid at room temperature, where, however, the splitting  $a = 18$  G (for the spectra of  $\dot{R}CFR'$  of the dicarboxylic acids, see Figs 2B and 2D).

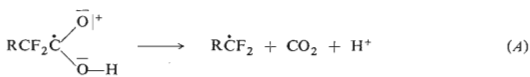
The center of the derivative spectrum of  $\dot{R}CFR'$  radicals should reflect the sharp decrease of the intensity of the absorption spectrum when the minimum splitting of  $F_\alpha$ , i.e. the minimum principal value of the tensor  $F_\alpha$  of the interaction  $A_{min}^{F\alpha} = 10 - 20$  G, is achieved. The middle principal value of the tensor is often identical or very close to the minimum principal value so that the tensor of  $F_\alpha$  interaction has an axial symmetry ( $a_{||}^F, a_{\perp}^F$ ) and the change of the intensity of the absorption spectrum at the minimum splitting of  $F_\alpha$  is larger than for the maximum splitting of  $F_\alpha$ . Moreover, in the center of the spectrum no similarity with the spectral edges can be expected because the splitting of  $F_\beta$  nuclei for the radical orientation at which  $A_{min}^{F\alpha}$  is reached differs from  $a^{F\beta}$  obtained at the orientation giving  $A_{max}^{F\alpha}$ . Moreover,  $A_{min}^{F\alpha}$  amounts to about 20 G so that structures, formed by the interaction with  $F_\beta$  nuclei, overlap. The simplification of centers of spectra at higher temperatures is caused by the higher freedom of radicals yielding or the isotropy of  $F_\beta$  interactions or the identity of  $A_{medium}^{F\alpha}$  with  $A_{min}^{F\alpha}$ .

## Mechanism of Radiolysis

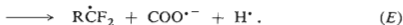
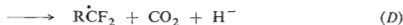
It is well known that the mechanism of radiolysis of aliphatic mono-<sup>15-17</sup> and dicarboxylic<sup>18,19</sup> acids comprises the formation of radical-anions, stable usually up to  $-183^{\circ}\text{C}$ . In conditions when the dimer structure of acids bound by hydrogen bonds is perturbed, *e.g.* by sorption<sup>20</sup> or in aqueous solutions<sup>17</sup>, radicals observed at 77 K have a general formula  $\text{R}\dot{\text{C}}\text{H}_2$  ( $\text{R} = \text{alkyl, H}$ ).

In mono- and dicarboxylic acids studied in this paper no formation of radical-anions has been observed after  $\gamma$ -irradiation at 77 K. In aqueous solutions of acids only the radicals  $\text{R}\dot{\text{C}}\text{F}_2$  have been identified, in acids there were also radicals  $\text{R}\dot{\text{C}}\text{FCOOH}$  and in salts at 77 K the  $\text{R}\dot{\text{C}}\text{FCOO}^-$  radicals were formed predominantly and the  $\text{R}\dot{\text{C}}\text{F}_2$  radicals were in minority. From this it follows that the ionized products of the interaction of the radiation with the molecule of the perfluoroacid decompose at a temperature lower than 77 K. The nature of their decomposition products depends, however, on the medium that surrounds the unstable radical-ions.

Radical-cations are the assumed precursors of the decarboxylation reaction (A) and the radical-anions can decompose to the  $\text{R}\dot{\text{C}}\text{FCOOH}$  radical and  $\text{F}^-$  according to (B)



Depending on the structure of the neighbourhood even other reactions of radical anions can be assumed, *e.g.* reactions (C), (D) and (E), which can explain the changing ratio of radicals  $\text{R}\dot{\text{C}}\text{F}_2$  and  $\text{R}\dot{\text{C}}\text{FCOOH}$  in samples of different acids.



The radical  $\text{COO}^-$  does not manifest itself in observable amounts in the spectra but the saturation experiments were not carried out and the hydrogen atoms recombine or react with neutral molecules at temperatures lower than 77 K so that the occurrence of decompositions according to Eqs (C), (D) and (E) can be judged only from the lower amount of  $\text{R}\dot{\text{C}}\text{FCOOH}$  radicals in comparison with the amount of  $\text{R}\dot{\text{C}}\text{F}_2$  radicals.

By heating, the radicals  $\text{R}\dot{\text{C}}\text{F}_2$  vanish in all cases by the abstraction of fluorine from the  $\alpha$ -carbon of acids or salts and give rise to the radicals  $\text{R}\dot{\text{C}}\text{FCOOH}$  or

$\dot{R}\dot{C}F\dot{C}OO^-$ . As far as the radicals  $\dot{R}\dot{C}F\dot{C}OOH$  or  $\dot{R}\dot{C}F\dot{C}OO^-$  were found after  $\gamma$ -irradiation at 77 K, they were formed immediately in the interaction of the radiation with the molecule because at 77 K both  $\dot{R}\dot{C}F_2$  and  $\dot{R}\dot{C}F\dot{C}OOH$  (or  $\dot{R}\dot{C}F\dot{C}OO^-$ ) radicals are stable.

The effect of water on the radiolysis remains unresolved. The presence of larger amounts of water in the acid prevents the formation of  $\dot{R}\dot{C}FR'$  radicals and also causes that the  $\dot{R}\dot{C}F_2$  radicals, as well as  $\dot{R}\dot{C}FR'$  radicals after heating, are more mobile (*cf.*  $CF_3CF_2COOH$ ) and therefore they are more reactive ( $\dot{R}\dot{C}F_2$  abstracts F atom at lower temperature than in the pure acid). The amount of OH radicals formed by the radiolysis of water should be very small because in the ESR spectra they would manifest themselves by an asymmetry of the central parts of spectra. Evidently, their reaction with an acid, similar to the abstraction of hydrogen in aliphatic acids, giving rise to  $\dot{R}\dot{C}HCOOH$ , cannot take place in perfluoro acids.

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