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Electron Spin Resonance of X-Irradiated Single Crystals of Zinc Acetate Dihydrate: Hindered Rotation of Methylene Group in a Free Radical CH_2COO^-*1

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Electron spin resonance spectra of X-irradiated single crystals of zinc acetate dihydrate have been studied at 9.2 Gc in the temperature range from 77°K to 380°K. The radicals trapped at 77°K are CH_3 and CH_2COO^-. The former disappears above 150°K. The latter is stable and persists up to 370°K. The principal values of hyperfine coupling constants for two indetical hydrogens of the radical CH_2COO^- have been found to be 10.5, 20.6 and 33.4G. The CH_2 group in the radical undergoes restricted rotation about the C–C bond. Analysis of the ESR spectra at different temperatures with a modified Bloch equation shows the activation energy and the frequency factor for the restricted rotation to be 5.8 ± 0.2 kcal/mol and $(4.4\pm2.7)\times10^{12}$ sec^{-1}, respectively.

Electron spin resonance (ESR) studies of free radicals have given valuable information on the structure of the radicals as well as their restricted motion. Changes in ESR spectra with temperature due to motion of free radicals have been found and analyzed in some irradiated organic substances. Methyl groups undergo restricted reorientation about a C–C bond in such radicals as CH_3-$CHCOOH$ trapped in alanine[1,2] and CH_3C-$(COOH)CH_2COOH$ trapped in itaconic acid[3]. Their rotation is nearly quenched below 100°K, but the methyl group of a radical $CH_3C(COOH)_2$ in irradiated malonic acid executes nearly free rotation even at 4.2°K.[4] Restricted torsional motion of a methylene group about a C–C bond has also been found in radicals trapped in an irradiated crystal of hexamethylenediammonium adipate,[5] in an irradiated mixed crystal of urea-fumaric acid[6] and in irradiated ethylmalonic acid and *n*-propylmalonic acid.[7] Reorientation of a terminal methylene group, however, has not been found in a radical of the type CH_2R within the knowledge of the present authors, except insufficient evidence for the reorientation motion in a radical CH_2COO^- trapped in an irradiated crystal of glycine.[8]

In this paper, the ESR studies of X-irradiated single crystals of zinc acetate dihydrate $Zn(CH_3COO)_2\cdot2H_2O$ are presented. The trapped radicals have been identified as CH_3 and CH_2COO^-. A marked temperature dependence has been found in the absorption spectra of the radical CH_2COO^-, from which it is concluded that the motion of the CH_2 group is quenched at low temperatures but undergoes rapid reorientation around the C–C bond above room temperatures. A quantitative analysis of the temperature dependence of the ESR spectra has been undertaken to give the activation energy and the frequency factor for the internal rotation of the radical in the crystal.

Experimental Procedures and Outline of the ESR Spectra

Single crystals of zinc acetate dihydrate were grown from the aqueous solution by slow evaporation. The crystal structure has been determined by Niekerk *et al.*[9]; the lattice is monoclinic with space group $C2/c$-C_{2h}^6, $a=14.5$, $b=5.32$, $c=11.02$ Å and $\beta=100.0°$ with four molecules per unit cell. The crystal axes were determined by comparing interfacial angles calculated from the lattice constants with those observed with an optical goniometer available from the Stoe Co. An orthogonal

*1 Presented at the 5th Symposium on Electron Spin Resonance, Sendai, Sept., 1966.

1) I. Miyagawa and K. Itoh, *J. Chem. Phys.*, **36**, 2157 (1962).
2) A. Horsfield, J. R. Morton and D. H. Whiffen, *Mol. Phys.*, **5**, 115 (1962).
3) M. Fujimoto, *J. Chem. Phys.*, **39**, 846 (1963).
4) C. Heller, *ibid.*, **36**, 175 (1962).
5) M. Kashiwagi and Y. Kurita, *ibid.*, **39**, 3165 (1963).
6) C. Corvaja, *ibid.*, **44**, 1958 (1966).
7) N. Tamura, M. A. Collins and D. H. Whiffen, *Trans. Faraday Soc.*, **62**, 1037 (1966); *ibid.*, **62**, 2434 (1966).
8) R. F. Weiner and W. S. Koski, *J. Am. Chem. Soc.*, **85**, 873 (1963); J. R. Morton, *ibid.*, **86**, 2325 (1964).
9) J. N. van Niekerk, F. R. L. Schoening and J. H. Talbot, *Acta Cryst.*, **6**, 720 (1953).

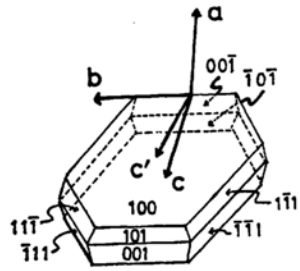


Fig. 1. The crystal form and the crystal axes of zinc acetate dihydrate. The orthogonal set of the *a*, *b* and *c'* axes are chosen for analysis of the ESR spectra.

set of the axes *a*, *b* and *c'* was chosen for the analysis of the spectra as shown in Fig. 1.

The crystals were exposed to X-rays (180 kV, 23 mA) to the extent of approximately 1 Mrad at 77°K. Second derivative ESR spectra were recorded with a Varian 4501 Spectrometer with 100 kc and 40 cps double field modulation. The spectra at 77°K were obtained for the irradiated crystal mounted in a quartz Dewar filled with liquid nitrogen for various orientations of the crystal. The spectra at various temperatures in the range from 77°K to 380°K were taken at two fixed field directions, parallel to the *c* axis and parallel to the direction which made an angle of +23° with the *a* axis in the *ac'* plane. The temperature control was achieved using a Varian V-4547 variable temperature equipment by passing heated or cooled nitrogen gas around the crystal. The temperature was measured with a copper-constantan thermocouple located near the crystal, with probable error of 3°C. ESR spectra of zinc acetate dihydrate powder irradiated at room temperature were also measured at various temperatures.

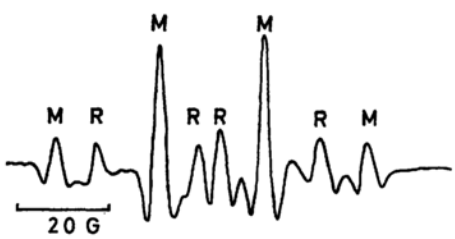


Fig. 2. Second derivative ESR spectra of a single crystal of zinc acetate dihydrate irradiated at 77°K. The spectra were obtained at 77°K for external magnetic field parallel to the *a* axis.

Figure 2 shows an ESR spectrum of the crystal irradiated at 77°K, which is measured immediately after the end of the irradiation, at the same temperature with magnetic field parallel to the *a* axis. The spectrum is composed of a quartet of peaks with equal spacings and with the intensity ratio of 1 : 3 : 3 : 1 (hereafter referred to as M for the sake of convenience), and a quartet (a doublet-doublet) of peaks with equal intensity (referred to as R). The integrated intensity of M is about twice as large as that of R. Above 150°K, the spectrum M disappears, while R persists up to 370°K where water of hydration is taken off. The pattern of R changes reversibly when the crystal is cooled or warmed in the temperature range from 77°K to 350°K. For the crystal irradiated at room temperature, only the spectrum R was observed at any temperature. The substitution of water of hydration by D_2O had no effect on the spectra except narrowing of the line width.

The spectrum M is essentially isotropic and its splitting is 23±1G. A paramagnetic species responsible for M is identified with no doubt as a methyl radical CH_3 which reorients rapidly. The same radical with coupling constants 21.8, 22.5, 22.5G was found in an X-irradiated sodium acetate trihydrate by Rogers and Kispert.[10] The spectrum R is highly anisotropic and its doublet splittings vary from 9 to 33G with the crystal orientation. It will be shown in the following section that the quartet R is attributable to a radical CH_2COO^-.

Analysis of ESR Spectra at Low Temperature and Structure of a Free Radical CH_2COO^-

Typical absorption spectra at 77°K are shown in Fig. 3 for the crystal irradiated at room temperature. In general, the spectra consist of two sets of quartets (doublet-doublet) with equal intensity, which coalesce into a quartet when the magnetic field

TABLE 1. PRINCIPAL ELEMENTS OF *g* FACTORS AND HYPERFINE SPLITTING CONSTANTS A^1 AND A^2 a)

Principal value		Direction consines with regard to the *a*, *b* and *c'* axis		
g_1	2.0013	0.726	∓0.639	0.252
g_2	2.0024	0.247	±0.585	0.773
g_3	2.0031	0.641	±0.499	−0.583
A_1^1	11.8 G	0.431	±0.730	0.530
A_2^1	20.6 G	0.781	∓0.596	0.185
A_3^1	33.3 G	0.451	±0.334	−0.827
A_1^2	9.1 G	0.176	∓0.040	−0.984
A_2^2	21.0 G	0.758	∓0.632	0.162
A_3^2	33.4 G	0.628	±0.774	0.082

a) The standard deviations are 0.0002 and 4° for the principal values and the principal axes of the *g* factors, respectively. For A^1 and A^2, they are 0.2 G and 1°, respectively.

10) M. T. Rogers and L. D. Kispert, *J. Chem. Phys.*, **46**, 221 (1967).

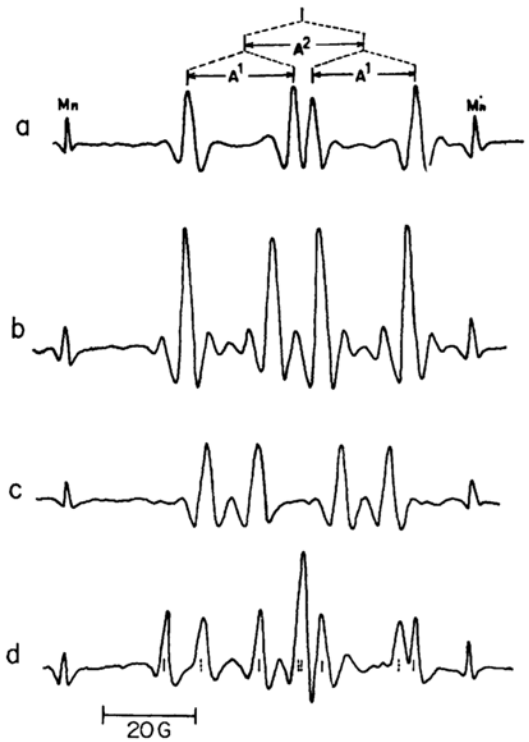


Fig. 3. Second derivative spectra of the crystal irradiated at room temperature and measured at 77°K with the magnetic field (a) parallel to the *a* axis, (b) parallel to the *b* axis, (c) parallel to the *c* axis and (d) at an angle of 30° from the *a* axis toward the *b* axis in the *ab* plane. The outermost lines are of Mn^{2+} in MgO powder which is used as field marker (spacing; 87.5 G).

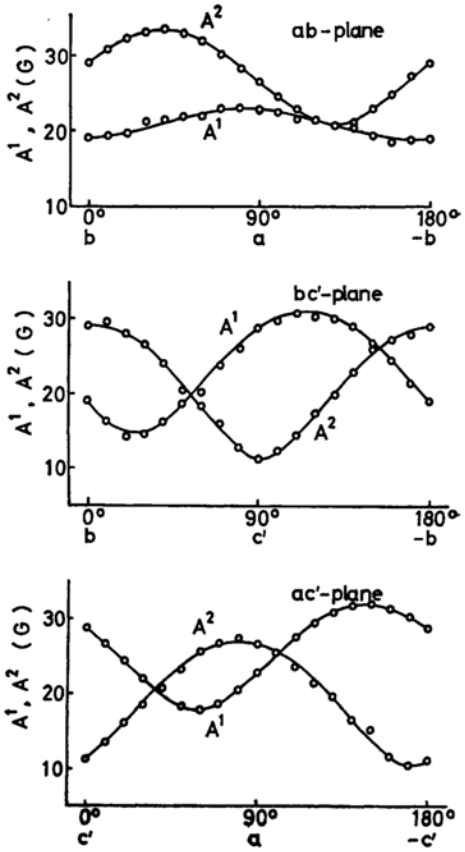
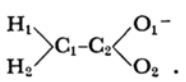


Fig. 4. Calculated (solid lines) and observed (circles) hyperfine splittings at low temperature with the magnetic field in the *ab*, *bc'* and *ac'* planes in a single crystal of zinc acetate dihydrate irradiated at room temperature. The angular dependences of A^1 and A^2 are illustrated for one of the two quartets observed with the magnetic field in the *ab* and *bc'* planes. A 180° rotation of the curves illustrated in the figure about the *b* axis gives the curves omitted.

is parallel to the *b* axis or in the *ac'* plane. The same spectra were obtained when the direction of the field is (l, m, n) or $(l, -m, n)$, where l, m and n are the direction cosines of the magnetic field with respect to the *abc'* system. These facts are compatible with the expectation that the two chemically equivalent but magnetically different radicals are trapped in the crystal with monoclinic symmetry.

It is evident that each quartet arises from two protons with different nuclear hyperfine coupling constants which are referred to as A^1 and A^2 as shown in Fig. 3. Figure 4 shows angular dependences of A^1 and A^2 observed when the magnetic field is in the *ab*, *bc'* or *ac'* planes. The observed data were analyzed by means of least mean square method with the aid of the second-order equations. The calculation was performed by an electronic computer. Table 1 shows the values determined for the principal elements of the tensors $\boldsymbol{A}^1$ and $\boldsymbol{A}^2$, and those of the spectroscopic splitting tensor $\boldsymbol{g}$. The angular dependences of A^1 and A^2 calculated from the results given in Table 1 are shown graphically in Fig. 4. The principal values of $\boldsymbol{A}^1$ and $\boldsymbol{A}^2$ are identical within the limit of experimental error. Therefore, the radical responsible for the spectrum R must contain CH_2 and is most likely



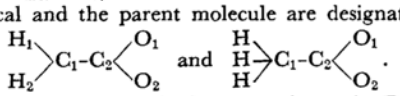
Further analysis confirms this identification. An unpaired electron is in the p_π orbital of the sp^2 configuration of C_1. In such a radical, it has been shown both theoretically and experimentally that the smallest g value ($\boldsymbol{g}_1$) should occur along the direction parallel to the symmetry axis of the p_π orbital (perpendicular to the radical plane) and the directions corresponding to the minimum, medium and maximum value of the principal elements of the hfs tensor are parallel to the C-H bond, parallel

TABLE 2. THE ORIENTATION OF THE RADICAL CH_2COO^- AND THE PARENT MOLECULE CH_3COO^- IN A CRYSTAL OF ZINC ACETATE DIHYDRATE[a)]

Direction	Vector[b)]	Direction cosine with respect to the *abc'* system[c,d)]			
C_1-C_2 (radical)	$(\boldsymbol{A}_1^1+\boldsymbol{A}_2^1)$	0.592	0.675	−0.443	$(\boldsymbol{n}_{r1})$
	$\boldsymbol{g}_3$	0.641	0.449	−0.583	$(\boldsymbol{n}'_{r1})$
C_1-C_2 (molecule)	From crystal structure[9)]	0.662	0.534	−0.531	$(\boldsymbol{n}_{m1})$
Normal to the plane of $H_1H_2O_1O_2$ (radical)	$(\boldsymbol{A}_1^1\times\boldsymbol{A}_1^2)$	0.792	−0.588	0.165	$(\boldsymbol{n}_{r2})$
	$\boldsymbol{g}_1$	0.726	−0.639	0.252	$(\boldsymbol{n}'_{r2})$
Normal to the plane of $O_1O_2C_1C_2$ (molecule)	From crystal structure[9)]	0.892	−0.446	0.115	$(\boldsymbol{n}_{m2})$

The angle between C_1-C_2 (radical) and C_1-C_2 (molecule) is 9° ($\angle\boldsymbol{n}_{m1}$, $\boldsymbol{n}_{r1}$) or 13° ($\angle\boldsymbol{n}_{m1}$, $\boldsymbol{n}'_{r1}$). The angle between the normal to the plane of $H_1H_2O_1O_2$ (radical) and that of $O_1O_2C_1C_2$ (molecule) is 9° ($\angle\boldsymbol{n}_{m2}$, $\boldsymbol{n}_{r2}$) or 16° ($\angle\boldsymbol{n}_{m2}$, $\boldsymbol{n}'_{r2}$).

a) The atoms in the radical and the parent molecule are designated as;



b) $\boldsymbol{A}_1^1$, $\boldsymbol{A}_1^2$, $\boldsymbol{g}_3$ and $\boldsymbol{g}_1$ represent the principal vectors shown in Table 1.

c) Of the two crystallographically unequivalent species, direction cosines are tabulated for one species.

d) Unit vectors having these direction cosines are designated as $\boldsymbol{n}_{r1}$, $\boldsymbol{n}'_{r1}$, *etc.*

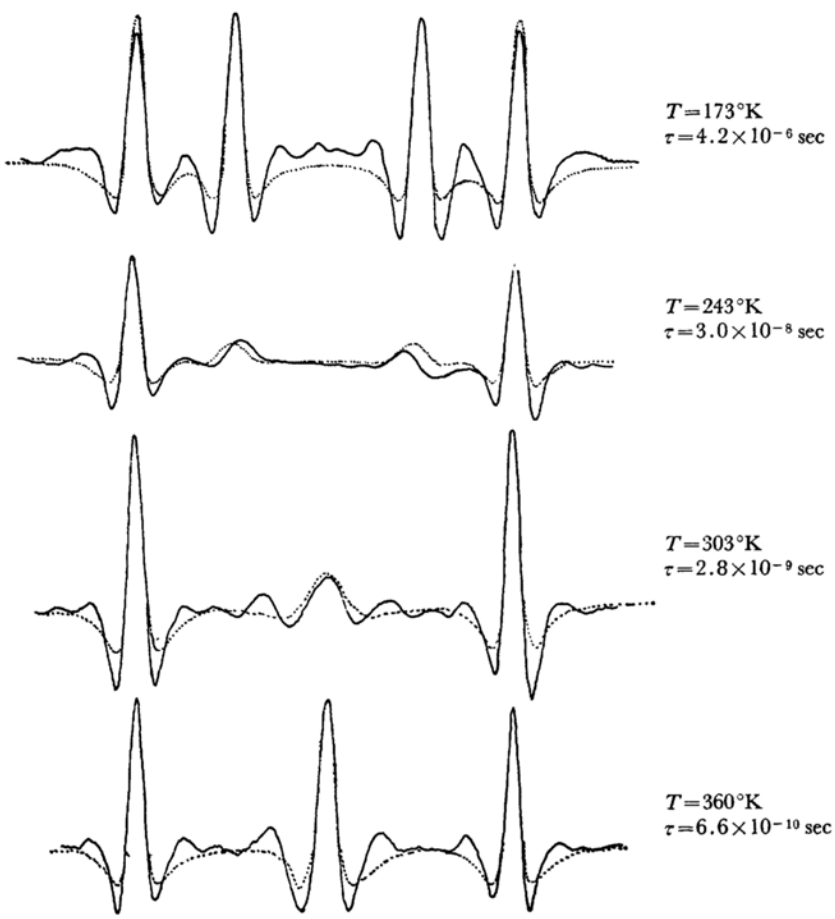


Fig. 5. Observed (solid lines) and calculated (dotted lines) second derivative ESR spectra of CH_2COO^- in the crystal for the magnetic field parallel to the c axis at different temperature T. The calculated spectra are obtained according to Eq. (2) together with Eq. (3) and the values of E and f_0 indicated in (4).

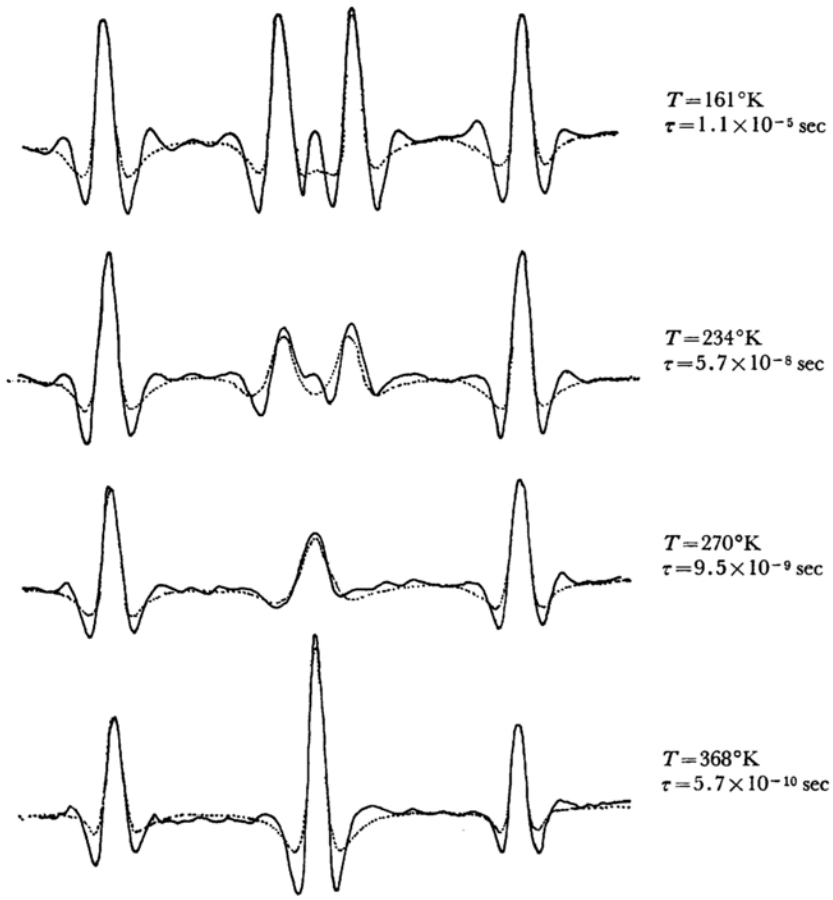


Fig. 6. Second derivative absorption curves of CH_2COO^- similar to Fig. 5, except that the applied magnetic field is in the ac' plane and makes an angle of 23° with the a axis toward the c' axis.

to the symmetry axis of the p_π orbital and perpendicular to these two directions, respectively.[11-13]

In addition, a symmetry consideration on the radical predicts that the direction of the C_1-C_2 bond is parallel to a bisector of the directions of the minimum principal values of $\boldsymbol{A}^1$ and $\boldsymbol{A}^2$ or is parallel to $\boldsymbol{g}_2$ or $\boldsymbol{g}_3$, where $\boldsymbol{g}_2$ and $\boldsymbol{g}_3$ are the medium and maximum principal elements of g tensor, respectively.

The direction of the C_1-C_2 bond and the normal to the plane $H_1C_1C_2H_2$ of the radical are determined from the values given in Table 1 and compared with the orientation of the parent molecule in the crystal which is determined by X-ray analysis.[9] The direction normal to the plane $H_1C_1C_2H_2$ (perpendicular to $\boldsymbol{A}_1^1$ and $\boldsymbol{A}_1^2$) agrees within 8° with the direction along the symmetry axis of p_π orbital (parallel to $\boldsymbol{g}_1$). The angle $\angle H_1C_1H_2$ (angle between $\boldsymbol{A}_1^1$ and $\boldsymbol{A}_1^2$) is obtained as $118°\pm3°$. As shown in Table 2, the direction of the C_1-C_2 bond of the radical agrees with that of the parent molecule. Moreover, the plane $H_1C_1C_2H_2$ of the radical is parallel to the plane $O_1O_2C_1C_2$ of the parent molecule. These facts indicate that the free radical is formed from the parent molecule CH_3COO^- by loss of a hydrogen atom followed by a reorientation of the CH_2 group to make a planar radical. The orientation of $O_1O_2C_2$ is unchanged when the loss of hydrogen occurs. The principal values of the hfs tensor of the radical CH_2COO^- trapped in a zinc acetate dihydrate crystal (10.4, 20.8, 33.4G) are nearly equal to those of the radical CH_2COO^- produced in glycine (10.3, 21.8, 32.5G),[14] and to those of CH_2COOH produced in malonic acid (11.9, 20.5, 32.6G).[15] It is concluded that the spin density on the α-carbon atom in these radicals is

11) H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960).
12) H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 108 (1957).
13) H. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959).
14) H. C. Box, H. G. Freund and E. E. Budinski, *J. Am. Chem. Soc.*, **88**, 658 (1966).
15) A. Horsfield, J. R. Morton and D. H. Whiffen, *Nature*, **189**, 481 (1961).

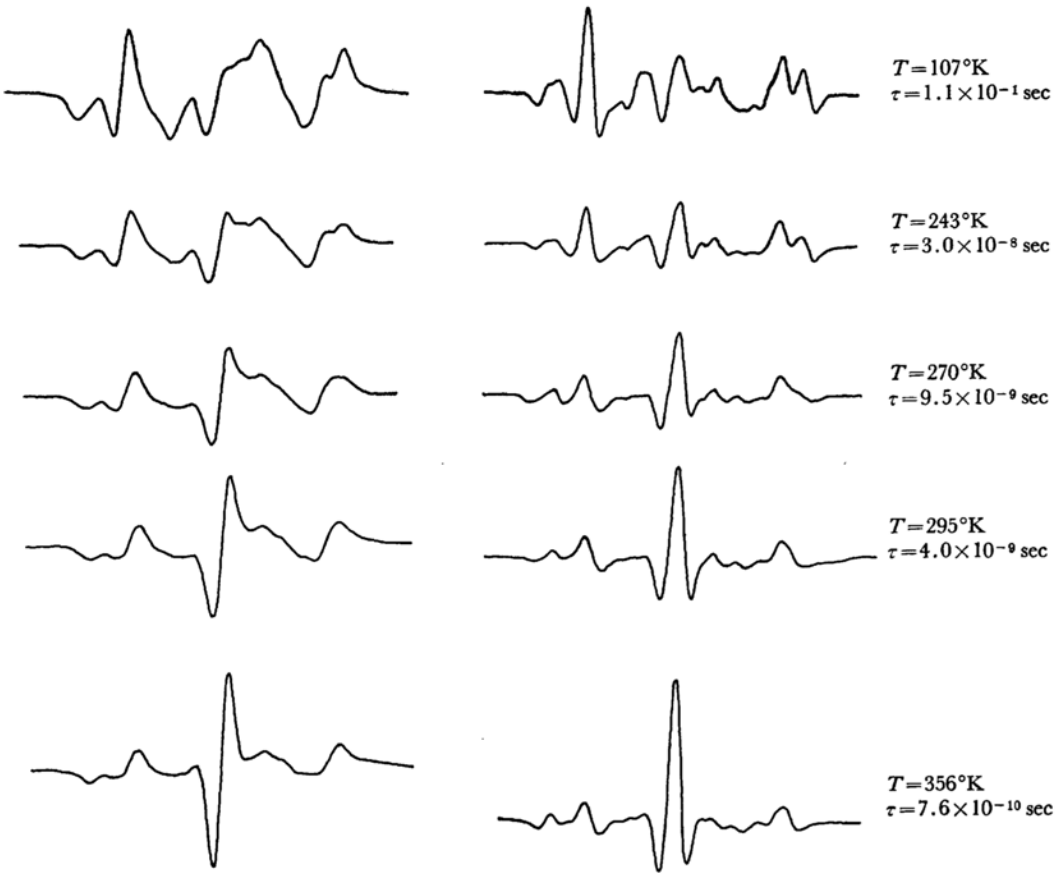


Fig. 7. Temperature dependences of the first (left side) and second (right side) derivative ESR spectra of CH_2COO^- trapped in X-irradiated zinc acetate dihydrate powder. The value of τ given in each spectrum is calculated from Eq. (3) with E and f_0 indicated in (4).

unaffected whether the COO group is linked with neighboring molecules by hydrogen bonds or makes ionic bonds with Zn^{2+}.

Temperature Dependence of ESR Spectra; The Hindered Rotation of CH_2 Group of CH_2COO^-

Figures 5 and 6 show the ESR spectra of CH_2COO^- recorded at various temperatures with the magnetic field in the *ac'* plane. In the temperature range from 77°K to 170°K the spectrum is composed of a quartet with equal intensity. At higher temperatures, the outer lines of the quartet are unchanged, whereas the inner lines become broadened, their peak heights decrease, and their separation also decreases. Near 270°K the inner lines practically disappear. At higher temperature a line appears at the center of outer lines and its intensity increases with increase of temperature and approaches twice the intensity of the outer lines. First and second derivative ESR spectra of CH_2COO^- trapped in zinc acetate dihydrate powder obtained at different temperatures are illustrated in Fig. 7 for comparison with the crystal ESR spectra.

The temperature dependence mentioned above is characteristic of the system in which the two hydrogen atoms exchange their sites with each other through a rotation of the CH_2 group about the C-C bond, the rate of the exchange increasing with increasing temperature. This is easily recognized qualitatively as illustrated in Fig. 8. If the reorientation rate, τ^{-1}, is much smaller than $|A^\alpha - A^\beta|$, the spectrum will be a quartet, where A^α and A^β are the hyperfine coupling constants in frequency unit of the protons located at equilibrium positions "α" and "β", respectively. The resonant frequencies of the quartet are $\nu_0 \pm |A^\alpha + A^\beta|/2$ (outer lines), corresponding to the nuclear spin states $(++)$ and $(--)$ of the two protons H_1 and H_2, and $\nu_0 \pm |A^\alpha - A^\beta|/2$ (inner lines), corresponding to $(+-)$ and $(-+)$, where ν_0 is the resonant frequency of the unpaired electron with no hfs and $(+-)$, for example, designates the state in which H_1 and H_2 have nuclear spin components of $+1/2$ and $-1/2$, respectively.

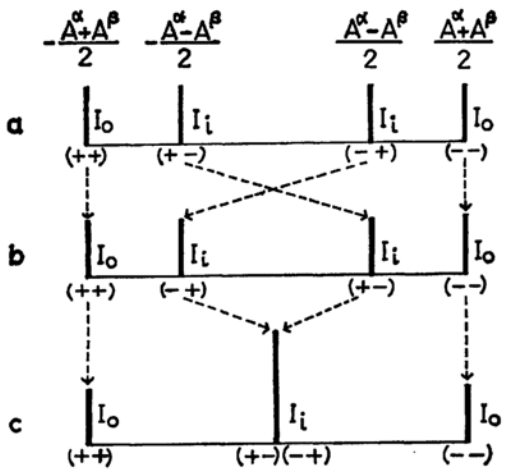


Fig. 8. Patterns of absorption spectra of CH_1H_2R.

(a) H_1 and H_2 are in the equilibrium positions "α" and "β", respectively.
(b) H_1 and H_2 exchanges their positions through rotation around the C-C bond. H_1 and H_2 are in "β" and "α", respectively.
(c) The methylene group undergoes rapid reorientation.

The relation $A^\alpha > A^\beta > 0$ is assumed.

When $\tau^{-1} \gg |A^\alpha - A^\beta|$, the spectrum is a triplet with the intensity ratio of 1 : 2 : 1, the resonant frequencies of which are $\nu_0 \pm |A^\alpha + A^\beta|/2$, corresponding to $(++)$ and $(--)$, and ν_0 which corresponds to $(+-)$ and $(-+)$. If τ^{-1} is comparable to $|A^\alpha - A^\beta|$, the positions and intensities of the outer lines are the same as those in the two cases mentioned above but inner lines become broadened and its separation becomes smaller than $|A^\alpha - A^\beta|$. These changes of the spectra with change of τ^{-1} is caused by the fact that the nuclear spin state of the protons is unchanged during the reorientation and, then, the inner lines exchange their positions with each other but the outer lines do not through the reorientation. The exchange or reorientation effects of protons on NMR spectra have been analyzed by Gutowsky and Holm[16] with modified Bloch equations. The effects of rotation of methyl group in a radical CH_3CHR on ESR spectra have been investigated with a similar procedure by Miyagawa and Itoh.[1] After their procedure, we analyzed numerically the second derivative ESR spectra of a radical with two protons which transfer between two sites.

If the splitting of the inner lines H_{spl}($|A^\alpha - A^\beta|$ in gauss) and the maximum slope line width

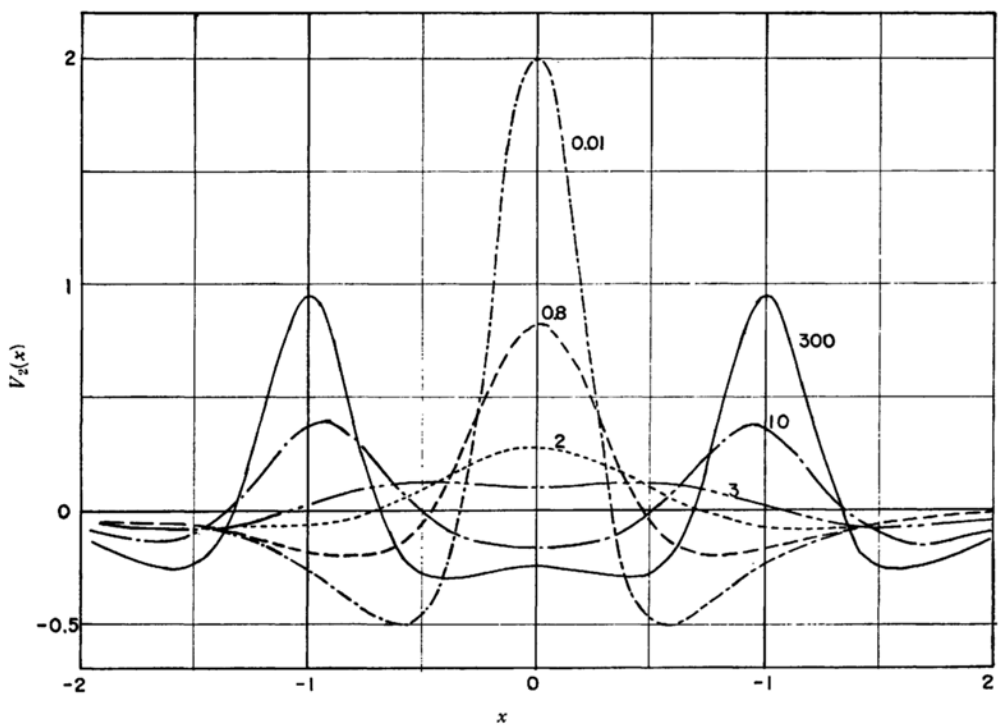


Fig. 9. Second derivative curves $V_2(x)$ for $r=0.33$ with different reduced exchange rates t. The values of t are given on each curves.

16) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); see also, J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York (1959), Chapt. 10.

ΔH_{msl}, both in the absence of the reorientation, are known, the spectra of the inner lines can be calculated for any given life time of the reorientation, τ. The absorption curve, V_0, is given as a function of reduced magnetic field x by the expression

$$V_0(x) = \frac{\sqrt{3}}{2} rt \,\mathrm{Real}\left\{\frac{f_\alpha + f_\beta}{1 - f_\alpha - f_\beta}\right\}, \tag{1}$$

and the second derivative of the absorption curves by

$$V_2(x) = \frac{3\sqrt{3}}{8} (rt)^3 \times \mathrm{Real}\left\{\frac{(f_\alpha - f_\beta)^2(f_\alpha + f_\beta - f_\alpha f_\beta) + f_\alpha f_\beta (f_\alpha + f_\beta)}{(1 - f_\alpha - f_\beta)^3}\right\} \tag{2}$$

where f_α and f_β are complex functions expressed as

$$\left.\begin{aligned} f_\alpha &= \left\{\frac{\sqrt{3}}{2} rt + 2 - i\frac{t}{2}(1 - x)\right\}^{-1} \\ f_\beta &= \left\{\frac{\sqrt{3}}{2} rt + 2 + i\frac{t}{2}(1 + x)\right\}^{-1} \\ &\qquad (i = \sqrt{-1}) \end{aligned}\right\} \tag{3}$$

where

$$x = \frac{2}{H_{spl}}(H - H_0),$$

$$r = \Delta H_{msl}/H_{spl},$$

and

$$t = \tau\gamma H_{spl}.$$

In the above expressions, H is applied magnetic field, H_0 is magnetic field at the center of the inner doublet and γ is electronic gyromagnetic ratio.

Line shape of each absorption line has been assumed to be Lorentzian and, therefore, $\Delta H_{msl} = 2/(\sqrt{3}\,\gamma T_2)$, where T_2 is spin-spin relaxation time. Equations (1) and (2) are normalized so as $V_0(\pm 1) = V_2(\pm 1) = 1$ when $\tau = \infty$. The maximum value of $V_2(x)$ is the ratio of the peak intensity of the inner line, I_i, to that of the outer line, I_o, which can be calculated from Eq. (2) as a function of τ for given r and H_{spl}.

At 77°K, τ is large enough to assume that the rotation of the CH_2 group of the radical CH_2COO^- does not take place practically and hence the linewidth and the separation between inner lines observed at this temperature can be taken as ΔH_{msl} and H_{spl}, respectively. The values of H_{spl} and ΔH_{msl} have been observed to be 20.1G and 2.52G ($r = 0.125$), respectively, for H parallel to the c axis, and to be 8.1G and 2.67G ($r = 0.33$), respectively, for the magnetic field parallel to a line which makes an angle of $+23°$ with the a axis in the ac' plane. Figure 9 shows the calculated spectra of the inner lines for several values of t

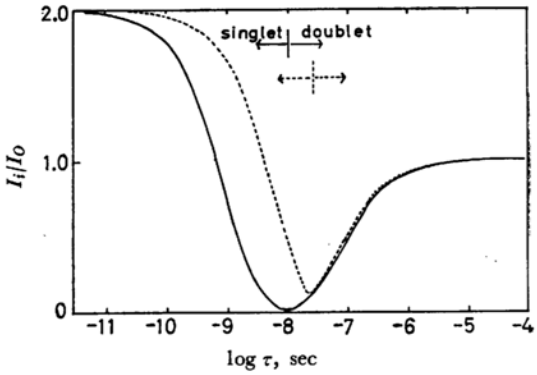


Fig. 10. Relation between τ and I_i/I_O for $H_{spl} = 20.1$ G and $\Delta H_{msl} = 2.59$ G ($r = 0.125$) (solid line) and for $H_{spl} = 8.1$ G and $\Delta H_{msl} = 2.67$ G ($r = 0.33$) (dotted line).

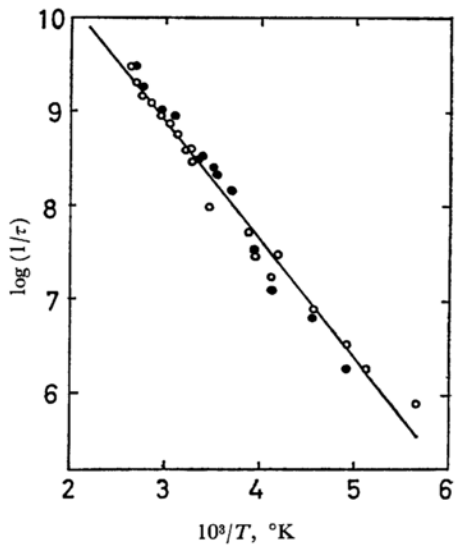


Fig. 11. Arrhenius plot of $1/\tau$ *versus* $1/T$. The straight line illustrates Eq. (3) with $E = 5.8$ kcal/mol and $f_0 = 4.4 \times 10^{12}$ sec^{-1}.
(○: $H_{spl} = 20.1$ G, $\Delta H_{msl} = 2.59$ G, ●: $H_{spl} = 8.1$ G, $\Delta H_{msl} = 2.67$ G)

for the case of $r = 0.33$. The ratios I_i/I_o calculated for $r = 0.125$ and $r = 0.33$ are shown in Fig. 10 as functions of τ. Comparing the quantities I_i/I_o observed at various temperatures with the calculated values, τ has been determined for the temperatures at which the spectra were obtained. The plots of $\log(1/\tau)$ *versus* $1/T$ are shown in Fig. 11. The linear relation between $\log(1/\tau)$ and $1/T$ indicates that τ follows the equation;

$$\frac{1}{\tau} = f_0 \exp(-E/RT), \tag{3}$$

where f_0 and E are interpreted as the frequency factor and activation energy for the rotation of the CH_2 group about the C_1-C_2 bond, respectively.

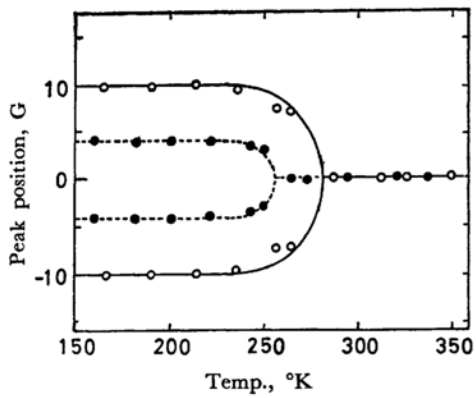


Fig. 12. Observed (dots) and calculated (lines) positions of the inner line peaks of the absorption spectra of CH_2COO^- in a zinc acetate dihydrate single crystal with varying temperature. The peak positions from the center of the spectra are measured in Gauss.
(○, ——: for $H_{spl}=20.1$ G and $\Delta H_{msl}=2.59$ G,
●, ----: for $H_{spl}=8.1$ G and $\Delta H_{msl}=2.67$ G)

The values for E and f_0 are found from Arrhenius plots in Fig. 11 as:

$$\left.\begin{aligned} E &= 5.8 \pm 0.2 \text{ kcal/mol} \\ f_0 &= (4.4 \pm 2.7) \times 10^{12} \text{ sec}^{-1}. \end{aligned}\right\} \quad (4)$$

In Figs. 5 and 6 the spectra calculated by Eqs. (2), (3) and (4) are illustrated with dotted lines for given temperatures. These figures show that the calculated spectra are in good agreement with the observed ones except tail parts of the absorption lines. The position of the inner line peaks has been calculated by the similar procedure as before and compared with the observation (Fig. 12). It is found in Fig. 12 that the observation is in good agreement with the calculation. The value of the frequency factor f_0 given in (4) is also in good agreement with 5.2×10^{12} sec^{-1} which is evaluated by the equation $f_0=\boldsymbol{k}T/\boldsymbol{h}$ based on the absolute rate theory,[17] where T is assumed to be 250°K. Lefebvre and Maruani[18] have calculated the absorption and first derivative spectra of randomly oriented CH_2COOH in which the methylene group rotate freely or is completely quenched arround the C-C bond (see Fig. 13 of their paper). It can be seen that Fig. 13 of their paper also reporduces the first derivative curves of the irradiated zinc acetate dihydrate powder (Fig. 7) in fair detail.

Disagreement of the calculated curves with the observed ones in the tail region (Figs. 5 and 6) arises from the following two reasons. Firstly, the calculation was carried out with an assumption that the shape function of each absorption line is Lorentzian but the real absorption line was nearly Gaussian. Secondly, the second-order effect or the "forbidden" transition was not taken into account, which was caused by a simultaneous transition of electronic and nuclear spins, though it was really observed in both sides of the absorption lines, as seen in Figs. 5 and 6.

For such radicals as $CH_2NHCONH_2$ (from methylurea),[19] CF_2CONH_2 (from trifluoroacetamide)[20] and CH_2COOH (from malonic acid),[15] the rotation of the CH_2 or CF_2 group does not occur even at room temperature. Activation energy of these groups is estimated to be higher than 9 kcal/mol. If it is assumed that $f_0=5\times10^{12}$ sec^{-1} and $H_{spl}=10$G, the lower energy than 9 kcal/mol would reveal the effect of the rotation on their ESR spectra. Therefore, it is of interest to examine, using a simple model, the cause of the fairly low activation energy for the CH_2 rotation in the case of CH_2COO^- in a crystal of zinc acetate dihydrate.

Now, we define θ as the angle between the plane $H_1C_1H_2$ and the plane $O_1O_2C_2$, and consider only an internal energy $V(\theta)$ of the radical which is a function of θ. $V(\theta)$ is a sum of the energies of five π-electrons $V_\pi(\theta)$ plus a repulsive energy $V_r(\theta)$ between the CH_2 and COO^- groups;

$$V(\theta) = V_\pi(\theta) + V_r(\theta). \quad (5)$$

$V_\pi(\theta)$ will be minimum at $\theta=0$ and π, and maximum at $\theta=\pi/2$ and $3\pi/2$, whereas $V_r(\theta)$ is maximum at $\theta=0$ and π, and minimum at $\theta=\pi/2$ and $3\pi/2$. The activation energy E for the rotation may be approximately $V(\pi/2)-V(0)$. With the simple Hückel MO method $V_\pi(\pi/2)-V_\pi(0)$ was calculated as follows.[21] Taking Coulomb energy for C_1, C_2, O_1 and O_2 to be α, $\alpha+0.2\beta$ $\alpha+2\beta$, and $\alpha+2\beta$, respectively, and taking the resonance energy for the C_1-C_2, C_2-O_1 and C_2-O_2 bonds to be $\beta\cos\theta$, $\sqrt{2\beta}$ and $\sqrt{2\beta}$, respectively, it is found that $V_\pi(\pi/2)-V_\pi(0)=-0.562\beta$. If β is taken as -18 kcal/mole,[21] which have been evaluated from the resonance energy for benzene, $V_\pi(\pi/2)-V_\pi(0)$ is 10.1 kcal/mol.

$V_r(\theta)$ is not known experimentally, but $V_r(0)-V_r(\pi/2)$ can be roughly evaluated as follows. Assuming the repulsive energy between a hydrogen atom and an oxygen atom is the same in CH_2COO^- and CH_3COOH, the activation energy for the hindered rotation of CH_2COO^- may be larger than that of the methyl group in CH_3COOH, which has been known to be 2.5 ± 0.7 kcal/mol.[22]

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This is because the height of two fold potential barrier (in the case of CH_2COO^-) is larger than that of three fold potential barrier (in the case of CH_3COOH). Thus, $V_\tau(0)-V_\tau(\pi/2)$ may be estimated without serious error as twice the activation energy for CH_3COOH, *i. e.*, 5.0 ± 1.4 kcal/mol. Therefore, the activation energy for the rotation of CH_2 in CH_2COO^- is $V(\pi/2)-V(0)=10.1-(5.0\pm1.4)$kcal/mol$=5.1\pm1.4$ kcal/mol, which is in good agreement with the observed value 5.6 ± 0.2 kcal/mol.

The agreement of the calculated activation energy with the observation for CH_2COO^- in a crystal of zinc actetate dihydrate suggests that the contribution of the surrounding molecules to the hindered rotation of the CH_2 group is negligibly small and that the activation energy is essentially determined by the internal energy of the radical. For the radicals of the type CH_2R having a high activation energy, however, the rotation of the CH_2 group may be hindered by the force acting on the radicals from the surrounding molecules in the crystals.

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