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Electron Spin Resonance of Irradiated Single Crystals of Sodium and Potassium 1-Oximinopropionates

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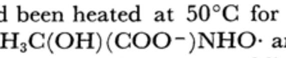
ESR studies have been made with single crystals of sodium 1-oximinopropionate irradiated at −196°C and at room temperature. The principal values and axes of the g and hyperfine tensors of the trapped radicals have been determined. The analysis of the observed data has indicated that the σ-electron radicals $CH_3C(COO^-)=NO\cdot$ are trapped at −196°C and at room temperature. It has been found that the electronic structures of the trapped radicals at these two temperatures are essentially the same, but that the environments of the radicals are very different from each other. After the crystal had been heated at 50°C for a week, the σ-electron radical vanished and the π-electron radicals, $CH_3C(OH)(COO^-)NHO\cdot$ and $CH_3CR'(COO^-)NRO\cdot$, appeared. The former may be formed in the solid state by adding a crystal water molecule to the unsaturated radical. The trapped radicals in irradiated single crystals of potassium 1-oximinopropionate were also studied at room temperature and after having been heated at 50°C. They are the σ-electron radical and the π-electron radical respectively, with structures similar to those of the sodium salt. The radical pairs have been observed in irradiated single crystals of the sodium salt at −196°C.

Electron spin resonance (ESR) studies of radicals trapped in irradiated single crystals of organic compounds have recently been carried out by many workers. Except for a few cases,[1,2] almost all the stable radicals trapped in irradiated carboxylic acids and amino acids are π-electron radicals produced by the removal of a proton or an amino group connecting with the carbon atom adjacent to the carboxyl group.[3] From this, it may be inferred that one of the factors necessary for the stabilization of the radicals is the participation of the carboxyl group in the π-conjugation. On the other hand, the trapped radicals in X-irradiated single crystals of dimethylglyoxime, $HON(CH_3)CC(CH_3)NOH$,[4] and glyoxime, HONHCCHNOH,[5] are the σ-electron radicals, the odd electron of which is localized on the lone-pair orbitals of the nitrogen and oxygen in the molecular plane. Since sodium 1-oximinopropionate,



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[1] Y. Kurita and W. Gordy, *J. Chem. Phys.*, **34**, 282 (1961).

[2] M. Katayama, *ibid.*, **37**, 2143 (1962).

[3] For example, H. M. McConnell and R. W. Fessenden, *ibid.*, **31**, 1688 (1959); N. M. Atherton and D. H. Whiffen, *Mol. Phys.*, **3**, 1 (1960); W. C. Lin and C. A. McDowell, *ibid.*, **4**, 333 (1961); I. Miyagawa and W. Gordy, *J. Chem. Phys.*, **32**, 255 (1960); T. S. Jaseja and R. S. Anderson, *ibid.*, **36**, 1098 (1962)

[4] I. Miyagawa and W. Gordy, *ibid.*, **30**, 1590 (1959).

[5] Y. Kurita, *Nippon Kagaku Zasshi*, *(J. Chem. Soc. Japan, Pure Chem. Sect.)* **86**, 581 (1965).

has a structure combining the above-mentioned two types of molecules, it is interesting to examine which type of radical is trapped stably in this crystal.

In almost all ESR studies of radicals trapped in single crystals, irradiation and measurements are conducted at room temperature on account of the available technical facilities. These measurements are thus restricted to a limited series of reactions in crystals. In the present study, we undertook to perform the irradiation of single crystals and the observation of ESR spectra at various temperatures, for the purposes of following the reaction of trapped radicals and of identifying the reaction products by the aid of the ESR technique.

The trapped radical in irradiated single crystals of potassium 1-oximinopropionate was also investigated, since the reactions studied here occur in the solid state and are expected to be sensitive to crystal structures.

Experimental

Pyruvic acid and hydroxylamine hydrochloride were used for the preparation of 1-oximinopropionic acid. The acid was then neutralized by an equivalent amount of sodium carbonate in an aqueous solution. The single crystal was grown from a saturated aqueous solution by slow evaporation at 20°C. It was very difficult to obtain a single crystal of sodium 1-oximinopropionate suitable for the ESR measurement.

Since the crystal structure of this crystal had never been reported, the crystallographic data were determined with the aid of an oscillation photograph and a Weissenberg photograph. The interfacial angles were also measured in order to confirm the analysis. The crystallographic data of sodium 1-oximinopropionate were determined as follows:

$a=13.71$ Å, $b=6.17$ Å, $c=6.65$ Å, $\beta=104.0°$,

$Z=4$, and the space group is $P2_1/c$.

A unit cell contains four water molecules besides the four oxime molecules. The calculated and observed densities were 1.739 and 1.730 (25°C) respectively.

Most of the crystals obtained had the plane form with well-developed faces. The flat plane is (100), and crystals are elongated along the c axis, as Fig. 1(a) shows. A new rectangular coordinate system, XYZ, was defined for the sake of convenience. The Y and Z axes are the same as the b and c axes of the crystal respectively, and the X axis is selected perpendicular to the YZ plane.

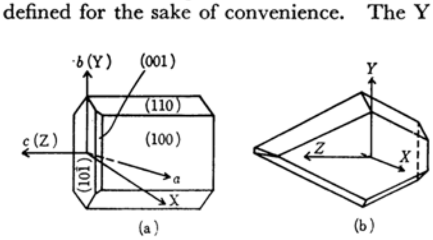


Fig. 1. The crystal forms and the coordinate axes employed.
(a) Sodium 1-oximinopropionate
(b) Potassium 1-oximinopropionate.

The deuterated specimens were also examined. The crystals which were grown from heavy water solutions had the same form as the ordinary ones. From the measurement of the 60 Mc proton nuclear magnetic resonance of the heavy water solution, it was found that all protons except for the methyl ones were deuterated. This was also confirmed by measuring the O–H and O–D stretching vibrations in the infrared region.

The single crystals of potassium 1-oximinopropionate were made by the same method as the sodium salt. No detailed analysis of the crystal structure of the potassium salt was performed. It is certain, however, that its lattice parameters are quite different from those of the sodium salt. The rectangular coordinate system, XYZ, was defined as is shown in Fig. 1(b). The Y and Z axes are taken in the flat plane of the crystal, and the X axis is taken to be perpendicular to them. The potassium salt crystal also contains crystalline water. It was found that all protons except for the methyl ones were deuterated when crystals were grown from heavy water.

The single crystals of sodium and potassium 1-oximinopropionates were exposed to γ-rays from 1000 Ci of ^{60}Co for six to seven hours. Sometimes X-rays operating at 30 kV and 15 mA were used for irradiation at room temperature, but no difference due to the irradiation source was detected. Upon such irradiation the colorless crystals turned yellow. The ESR spectra were measured with a Hitachi X-band spectrometer with 100 kc field modulation. All the spectra were recorded as second derivatives.

Free Radicals Trapped in Irradiated Sodium 1-Oximinopropionate

The Features of the ESR Spectra. The trapped radical, L, produced by irradiation at

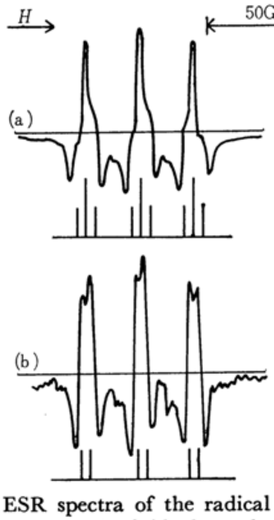


Fig. 2. ESR spectra of the radical L at −196°C with the magnetic field along the c axis.
(a) Sodium 1-oximinopropionate
(b) Deuterated sodium 1-oximinopropionate

−196°C showed spectra with a hyperfine structure (hfs) due to one nitrogen, N_L, and two hydrogens, H_{La} and H_{Lb}, as is shown in Fig. 2(a). The ESR spectra showed a pair of absorptions due to the radicals with two different orientations for the magnetic field in the XY and YZ planes. When a deuterated crystal was used, the hyperfine splitting due to one of the two hydrogens, H_{La}, was not observed: the hfs thus originates from only N_L and H_{Lb} (Fig. 2(b)).

When the crystal irradiated at −196°C was warmed to room temperature, the ESR spectra changed and gave the same spectra as those observed by irradiation at room temperature radical R. When this crystal was again cooled to −196°C, the ESR spectra remained unchanged.

The trapped radical, R, at room temperature gives the hfs due to one nitrogen, N_R, and one hydrogen, H_R, as is shown in Figs. 3(a) and 3(b). This is also the case for a deuterated crystal.

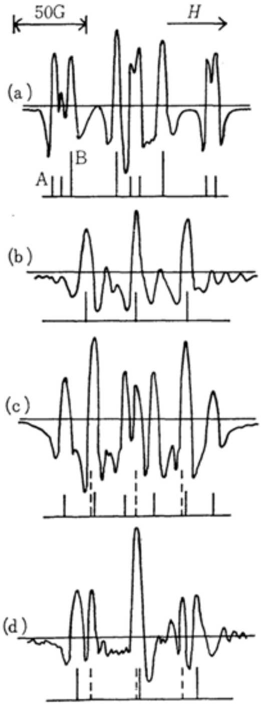


Fig. 3. ESR spectra of the normal and deuterated sodium 1-oximinopropionate measured at room temperature. Spectra (a) and (b) show the spectra of the radical R in a normal crystal with the magnetic field along the directions rotated 30° from the c to a axes in the ac plane and along the c axis, respectively. A and B in (a) indicate the two groups of lines due to the radical with the different orientations in crystal. Spectra (c) and (d) show the spectra of the radical W (full lines) and the radical V (broken lines) with the magnetic field along the c axis in the normal and deuterated crystals, respectively, after heating at 50°C for a week.

After the crystal irradiated at room temperature had been heated at 50°C for about a week, the above-mentioned spectra of the radical R disappeared and the new spectra shown in Figs. 3(c) and 3(d) appeared. After heating, the ESR spectra were measured at room temperature. The ESR spectra after heating were less intense than those before heating. The hfs of the former indicates the presence of two species of radicals with approximately the same concentration. The one, the V radical, gives the hfs due to only one nitrogen, N_V, as is shown by broken lines in Figs. 3(c) and 3(d). The other, the W radical, gives the hfs due to one nitrogen, N_W, and one hydrogen, H_W, as is shown by the full lines in Fig. 3(c). When a deuterated crystal was used, the W radical showed the hfs with broad absorption lines which is due to the only one nitrogen, N_W, as is shown in Fig. 3(d).

The above features can be summarized schematically as follows:

$$\begin{array}{lcccl}
-196°\text{C} & & \text{RT} & & \quad 50°\text{C} \\
(\text{L}) & \longrightarrow & (\text{R}) & \longrightarrow & (\text{V})+(\text{W}) \\
\text{N}_\text{L} & & \text{N}_\text{R} & & \text{N}_\text{V}\ \ \text{N}_\text{W} \\
\underline{\text{H}_\text{La}}\ \text{H}_\text{Lb} & & \text{H}_\text{R} & & \qquad \underline{\text{H}_\text{W}}
\end{array}$$

The underlining means that these hydrogens are replaced by deuterium when deuterated crystals are used.

An Analysis of the Spectra. The principal axes and values of the g tensors and the hyperfine coupling tensors (A tensors) were determined from the spectra which were observed with 10° intervals in the XY, YZ, and ZX planes. The spectra were analyzed by considering the nuclear Zeeman terms. The analyses were carried out with the aid of the least-squares method, using a Facom 202 electronic computer. The results are shown in Tables 1 and 2. The suffixs are defined in the order of the magnitude of the principal values as follows; $|g_1|<|g_2|<|g_3|$ and $|A_1|>|A_2|>|A_3|$. All the A tensors due to the nitrogen are almost cylindrically symmetric, and the axis of symmetry may be parallel to the axis of the 2p orbital of the nitrogen which is occupied by the odd electron.

According to the simple molecular orbital theory, the wave function of the odd electron orbital can be represented by a linear combination of the hybridized orbital of nitrogen, ϕ_N, and those of the other atoms, ϕ_i:

$$\Psi = (\rho_N)^{1/2}\phi_N + \sum_i(\rho_i)^{1/2}\phi_i \qquad (1)$$

where $\phi_N = a\chi^N_{2s} + b\chi^N_{2p}$ and $a^2+b^2=1$. The functions χ^N_{2s} and χ^N_{2p} indicate the atomic 2s and 2p orbitals of the nitrogen respectively. Following the method of Miyagawa and Gordy,[4] the s character, S, of the ϕ_N orbital, and the odd

TABLE 1. PRINCIPAL VALUES AND AXES OF THE g AND A TENSORS OF THE RADICAL R AND L

Principal axes	Principal values*	Direction cosines		
		X	Y	Z
g_1(R)	2.0024±0.0002	0.770	±0.638	−0.021
g_2(R)	2.0069±0.0001	−0.009	±0.043	0.999
g_3(R)	2.0086±0.0001	−0.638	±0.769	−0.039
$A_1(N_R)$	43.2±0.3	0.892	±0.445	−0.078
$A_2(N_R)$	24.5±0.3	−0.117	±0.393	0.912
$A_3(N_R)$	22.5±0.4	−0.437	±0.804	−0.403
$A_\parallel(H_R)$	3.0±0.5	0.31	±0.31	0.90
$A_\perp(H_R)$	−1.5±0.5		$\perp$ $A_\parallel(H_R)$	
g_1(L)	2.0022±0.0001	0.863	±0.503	−0.045
g_2(L)	2.0067±0.0002	0.012	±0.069	0.998
g_3(L)	2.0089±0.0002	−0.504	±0.862	−0.053
$A_1(N_L)$	47.3±0.7	0.914	±0.404	−0.027
$A_2(N_L)$	25.8±0.3	−0.032	±0.138	0.990
$A_3(N_L)$	23.9±0.5	−0.404	±0.904	0.138
$A_1(H_{La})$	5.1±0.5	0.50	±0.87	0
$A_2(H_{La})$	−1.7±0.5	−0.87	±0.50	0
$A_3(H_{La})$	−2.6±0.5	0	0	1
$A_\parallel(H_{Lb})$	3.5±0.5	0	0	1
$A_\perp(H_{Lb})$	−0.9±0.5		$\perp$ $A_\parallel(H_{Lb})$	

* Principal values of the A tensors are in gauss.

TABLE 2. PRINCIPAL VALUES AND AXES OF THE g AND A TENSORS OF THE RADICAL W AND V

Principal axes	Principal values*	Direction cosines		
		X	Y	Z
g_1(W)	2.0024±0.0004	0.006	±0.235	0.972
g_2(W)	2.0071±0.0005	0.999	∓0.015	−0.003
g_3(W)	2.0077±0.0008	0.014	±0.972	−0.235
$A_1(N_W)$	31.0±1.0	−0.197	±0.271	0.942
$A_2(N_W)$	13.3±1.8	0.248	±0.944	−0.219
$A_3(N_W)$	8.0±1.5	0.948	∓0.191	0.253
g_1(V)	2.0027±0.0004	0.030	±0.168	0.985
g_2(V)	2.0069±0.0009	−0.095	±0.982	−0.164
g_3(V)	2.0072±0.0010	0.995	±0.089	−0.046
$A_1(N_V)$	24.3±0.8	−0.040	±0.420	0.907
$A_2(N_V)$	10.5±0.9	0.994	±0.105	−0.005
$A_3(N_V)$	7.8±1.2	−0.097	±0.901	−0.422

* Principal values of the A tensors are in gauss.

TABLE 3. FERMI TERMS (A_f), S CHARACTERS (S), AND ODD ELECTRON DENSITIES ON THE NITROGEN (ρ_N) OF THE TRAPPED RADICALS

Radical	A_f in gauss	S	ρ_N
R	30.1	0.124	0.44
L	32.3	0.118	0.50
W	17.4	0.074	0.43
V	14.3	0.080	0.32
KR	30.5	0.127	0.44
KH	16.4	0.063	0.48

electron density, ρ_N, of the nitrogen were calculated as is shown in Table 3, where

$$S = a^2 \tag{2}$$

$$\frac{a^2}{b^2} = \frac{3(A_\parallel + 2A_\perp)\langle r^{-3}\rangle_{2p}}{[20\pi(A_\parallel - A_\perp)\,|\chi_{2s}^{N}(0)|^2]} \tag{3}$$

$$\rho_N = \frac{(A_\parallel + 2A_\perp)}{[8\pi S(g\beta\mu_N/I_N)\,|\chi_{2s}^{N}(0)|^2]} \tag{4}$$

$A_\parallel$ is equal to A_1(N) and $A_\perp$ is taken as $[A_2(\text{N})+A_3(\text{N})]/2$. The parameters, $\langle r^{-3}\rangle_{2p}$ and $|\chi_{2s}^{N}(0)|^2$, were taken to be 3.10 a. u. and 4.77 a. u. respectively. They are Mayer's value[6] as caluclated by the SCF method.

The Radical R Trapped at Room Temperature. It is unlikely that the R radical is the π-electron radical in which the odd electron occupies the π-orbital delocalized over the molecular framwork, because there appeared no hyperfine coupling due to the methyl protons. Miyagawa and Gordy concluded the D radical produced by the γ-irradiation of dimethylglyoxime at room temperature to be the σ-electron radical.[4] The principal values of the D radical are $A_1=45\pm1$G, $A_2=A_3=25\pm1$G, $g_1=2.0026\pm0.0003$, $g_2=2.0063\pm0.0003$, and $g_3=2.0095\pm0.0003$. These values are similar to those of the R, radical, shown in Table 1. The angles between the principal axes are also similar to each other in these two radicals, as is shown in Table 4. The fact that the observed odd electron density (0.44) on the nitrogen atom is larger than that (0.31) evaluated by the simple Hückel method on the assumption of the π-electron radical also supports this conclusion (Table 3).

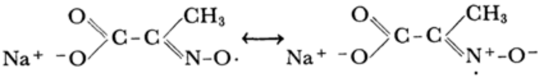
TABLE 4. ANGLES BETWEEN THE PRINCIPAL AXES

Angle	Radical D*	Radical R	Radical L	Radical W
$\angle A_1$(N) g_1	11°	14°	6°	12°
$\angle A_1$(N) g_2	89°	94°	89°	102°
$\angle A_1$(N) g_3	109°	103°	96°	88°
$\angle A_2$(N) g_2	—	22°	5°	76°
$\angle A_3$(N) g_3	—	24°	8°	103°

* Calculated from the data in Ref. 4.

The above-mentioned facts strongly suggest that the R radical in the sodium 1-oximinopropionate crystal is also the σ-electron radical, in the senses that the odd electron occupies the orbital composed of the lone-pair electron orbitals of the nitrogen and oxygen which are in the molecular plane and that its distribution is restricted to these two orbitals.

The hydrogen, H_R, which gives a small hfs is not the one bonded to the oxygen in the cation radical (C=N⁺–OH) proposed by Miyagawa and Gordy.[4] This is because the coupling due to this hydrogen remained unchanged when a deuterated crystal was used. This hydrogen is also not one of the methyl hydrogens, because the quartet hfs with the intensity ratio of 1 : 3 : 3 : 1 expected as a result of the rapid internal rotation at room temperature can not be observed. The mean distance between the odd electron and this hydrogen was found to be about 2.7 Å from the dipole-dipole (anisotropic) term. From the above-mentioned facts, it may be seen that this radical is a neutral radical with a planar configuration produced by the scission of the O–H bond.



The simple molecular orbital theory predicts the relation between the g tensor and the structure of the radical. The x and z axes are defined along the lone-pair orbital of the nitrogen, which is designated as h_x, and along the π orbital of the radical respectively. The x component of the lone-pair orbitals of the oxygen interacts with the orbital h_x, and they form the bonding and anti-bonding orbitals, ϕ, and ϕ^*, respectively. On the other hand, the y component of the oxygen lone-pair orbitals, σ_y, has no interaction. Among the six π-electron orbitals of the skeleton, four of them are occupied by eight π electrons. The highest occupied π-electron orbital and the lower three occupied orbitals are designated as π^* and π, respectively. The ground configuration of this σ-electron radical is $(\pi)^6(\phi)^2(\sigma_y)^2(\pi^*)^2(\phi^*)^1$. The order of the energy level may be $\phi^*>\pi^*>\sigma_y$ because this radical is the σ-electron radical.

As is well known, the elements of the g tensor are given by[7]:

$$g_{ij}=g_e[\delta_{ij}-\sum{}'\langle 0|\lambda^N l_i^N+\lambda^O l_i^O|n\rangle\langle n|\lambda^N l_j^N + \lambda^O l_j^O|0\rangle/(\mathrm{E}_n-\mathrm{E}_0)] \tag{5}$$

where $|0\rangle$ and $|n\rangle$ denote the ground and the n-th excited electronic states respectively, where λ and l denote the spin-orbit coupling constant and the orbital angular momentum operator, respectively, and where i and j denote x, y, and z. We take the x, y, and z axes as the principal axes here, so that g_{ij} with $i\neq j$ is zero. According to Eq. (5), it may be expected that the g_{yy} value to which the excitation from π^* to ϕ^* contributes predominantly is a maximum, that the g_{zz} value to which the excitation from σ_y to ϕ^* contributes predominantly is intermediate, and that the g_{xx} value which has nearly a free spin value is a minimum. The relation between the principal elements and the molecular structure was confirmed in the case of dimethylglyoxime,[4] since the molecular structure of the crystal is known for this compound. Though no crystal structure analysis of sodium 1-oximinopropionate has yet been made, the same relation should be satisfied if the R radical is the σ-electron radical; *i. e.*, the g_1 which is in the molecular plane is parallel to $A_1(N_R)$, g_2 is perpendicular to the molecular plane, and g_3 is in the molecular plane and perpendicular to g_1 and g_2.

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6) M. C. R. Symons, *Advances in Phys. Org. Chem.*, **1**, 332 (1963).

7) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.*, **A205**, 135 (1951); A. J. Stone, *ibid.*, **A271**, 424 (1963); C. P. Slichter, "Principles of Magnetic Resonance," Harper & Pow, Publishers, Inc., New York (1963), Chapter 7.

On the basis of the s character obtained from the hyperfine tensor of the nitrogen (Table 3), the odd electron orbital on the nitrogen, ψ_N, can be written as:

$$\psi_N = (0.124)^{1/2}\chi_{2s}^N + (0.876)^{1/2}\chi_{2px}^N \qquad (6)$$

On the other hand, the orbitals of the nitrogen bonded to the carbon and oxygen atoms are given by:

$$\psi_N{}^{\pm} = [(0.876)^{1/2}\chi_{2s}^N - (0.124)^{1/2}\chi_{2px}^N \pm \chi_{2py}^N]/(2)^{1/2} \qquad (7)$$

if the s character of the π orbital of the nitrogen is neglected and the two bonding orbitals are assumed to be equivalent. From the s and p characters of the two bonding orbitals, the bond angle, ∠CNO, is found to be 142°C for the R radical. On the basis of the foregoing discussion, the molecular plane and the C–N–O group of the radical can be located with reference to the crystal coordinate system XYZ, as is shown in Fig. 4.

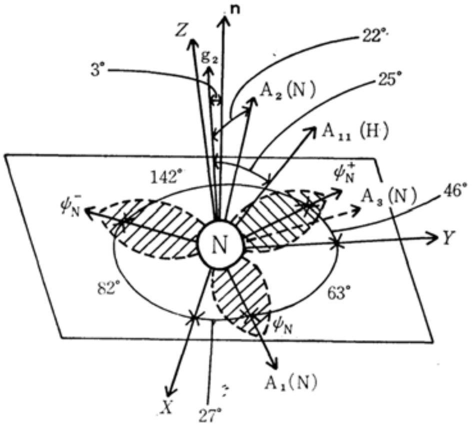


Fig. 4. The diagram indicating the orbital and the principal axes of the hyperfine tensors of the nitrogen and hydrogen of the radical R in irradiated sodium 1-oximinopropionate. The plane and the vector **n** are the molecular plane and its normal, respectively.

The L Radical Trapped at −196°C. As is shown in Table 1, the g and A(N) tensors of the L radical are similar to those of the R radical. This indicates that the two radicals have a similar electronic structure. Therefore, the L radical may also be the σ-electron radical. Following the procedure used for the R radical, the angles between the principal axes were found to be as is shown in Table 4. According to these data, it can be seen that there is only a small difference between these two radicals. This is not due to the molecular motion, because the R radical did not change its ESR spectra when cooled to −196°C. Table 4 shows that the angles between the g_2 and A_2(N) directions of the R and L radicals are 22° and 5° respectively. The direction of A_2(N) is expected to be perpendicular to the molecular plane, since the dipole-dipole interaction between the adjacent atoms contributes very little to the directions of the principal axes of A(N). The bond angle between the bonding orbitals of the nitrogen atoms is 142° for the L radical.

Neither of the two hydrogens giving the observed hfs is the hydrogen connecting to the oxygen in this case. The hfs due to H_{Lb} was not affected by the deuteration, while that due to H_{La} disappeared in a deuterated crystal. Therefore, H_{La} may be expected to be the hydrogen of the OH group. However, the observed principal values and directions of H_{La} are not consistent with the above expectation. The hydrogen of the OH group has its Fermi contact term by hyperconjugation. Since the observed Fermi term is very small, the bond direction of O–H must be nearly perpendicular to the molecular plane. On the other hand, the observed principal axis of $A_1(H_{La})$ with the largest principal value is in the molecular plane and nearly parallel to the odd electron orbital of the nitrogen. Therefore, the L radical may be concluded to be a neutral radical, as in the case of the R radical.

The hydrogen, H_{Lb}, which was not replaced by deuterium is not the methyl hydrogen, because the axis of the symmetry of the hyperfine coupling is nearly perpendicular to the molecular plane. On the other hand, the mean distances between the odd electron and hydrogens, H_{La} and H_{Lb}, were estimated from the dipole-dipole term to be about 2.3 Å and 2.5 Å respectively. Considering the small Fermi terms and the long distances from the odd electron, the hydrogens, H_{La} and H_{Lb}, are not intramolecular ones but intermolecular ones: probably H_{La} originates from the hydrogen of the oxime group of the neighboring molecule or that of water, and H_R and H_{Lb} have their source from a methyl hydrogen of the neighboring molecule or its reaction products.

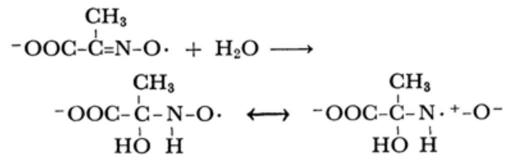
The Radicals Trapped at 50°C. Of the two radicals trapped after heating at 50°C, the W radical with the hfs due to one nitrogen, N_W, and one hydrogen, H_W, will be discussed first. From Tables 1, 2, 3 and 4, it may be seen that the electronic structure of this radical is quite different from that of the R radical. First, the magnitude of the Fermi term due to the nitrogen, N_W, of the W radical is smaller than that of the R radical. Second, the principal axes of the g and A(N) tensors of the W radical have different directions from those of the R radical. Third, the s character of the nitrogen is smaller than that of the R radical. On the other hand, the dipole-dipole term and the odd electron density on the nitrogen, ρ_N, are nearly the smae as those of the R radical. In addition to this, the hfs due to the methyl protons was not observed.

Recently, McConnell *et al.*[8] reported the results of their study of the g and nitrogen hyperfine tensors of the nitroxide π-electron radicals in single crystals. Let us take the di-*t*-butyl nitroxide radical as an example of the three radicals studied by them. Taking its principal axes, x, z and y, parallel to the N–O bond parallel to the π orbital of nitrogen, and perpendicular to them, respectively, McConnell *et al.* determined the A_{xx}, A_{yy}, A_{zz}, g_{xx}, g_{yy} and g_{zz} values of this radical to be 7.1±0.5G, 5.6±0.5G, 32±1.5*G*, 2.0089±0.0003, 2.0061 ± 0.0003, and 2.0027 ± 0.0003, respectively. These values are very similar to the corresponding values obtained with the W radical by the present authors (see Table 2). Furthermore, the magnitude of the Fermi term of the nitrogen of the W radical is similar to those of the π-electron radicals in solution formed by the oxidation of disubstituted nitric oxides with no conjugated system[9] (16—17G), as is shown in Tabel 3.

The above-mentioned facts suggest that the W radical is a π-electron radical. As for the directions of the principal axes, $g_1(W)$ and $A_1(N_W)$ are nearly parallel to each other, as is shown in Table 4. They are nearly parallel to $g_2(R)$, which was assumed to be perpendicular to the molecular plane. This indicates that the orbital occupied by the odd electron of the W radical takes the direction perpendicular to the molecular plane, since it seems unlikely that a large group such as $-C(CH_3)N\dot{O}$ changes its plane by nearly 90° in the crystal. This fact is also coincident with the findings on the π-electron radical reported by McConnell *et al.*

According to the theory of McConnell,[10] the Fermi term of the hydrogen coupling constant of the π-electron radical which has the $-\dot{N}H-$ structure is negative. The three principal axes of the hyperfine tensor of the hydrogen are along the N–H bond, the axis of the π-electron orbital, and the direction perpendicular to them. From the experiment of Rowlands,[11] it was found that the principal values are 8.8G, −21.2G, and −38.2 *G*, respectively when the odd electron is localized on the nitrogen.

Because of the complexity of the ESR spectra of the radicals after heating at 50°C, the principal values and axes of the coupling constant of the doublet were not determined very accurately. However, the observed doublet separation was at a minimum nearly along the X axis (less than 4*G*), and varied from 10 to 20 in the YZ plane. Thus the principal values are nearly 4, 10 and 20 G. These values coincide well with the experimental results of Rowlands if nearly half of the odd electron is on the nitrogen. This indicates that the Fermi term is negative. When a deuterated crystal was used, the splitting came within the line width. Therefore, this hydrogen was assigned to the N–H hydrogen. The most probable structure of the W radical is $CH_3C(COO^-)(OH)NHO\cdot$, which may be formed by the addition of a water molecule to the double bond of N=C as follows;

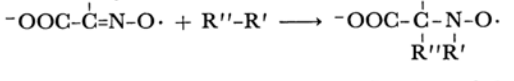


$${}^-OOC\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}N\text{-}O\cdot + H_2O \longrightarrow$$
$${}^-OOC\text{-}\underset{\displaystyle HO}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}\text{-}\underset{\displaystyle H}{\underset{|}{N}}\text{-}O\cdot \longleftrightarrow {}^-OOC\text{-}\underset{\displaystyle HO}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}\text{-}\underset{\displaystyle H}{\underset{|}{N}}\cdot{}^+\text{-}O^-$$

The hfs due to the methyl and hydroxyl hydrogens are expected not to be observed because they are situated three bonds away from the nitrogen. It can be seen from the principal values and the axes of the nitrogen and hydrogen hyperfine tensors that the N–H bond direction is along the X axis and that the π-electron orbital is along the direction of $A_1(N_W)$.

The ground state of the electronic configuration of this radical may be approximately represented by $(\phi_N)_2\ (\sigma_x)^2\ (\sigma_y)^2\ (\pi)^2\ (\pi^*)$, where ϕ_N, σ_x and σ_y are the bonding orbital of the N–H bond and the two lone-pair orbitals of the oxygen, respectively, and where π and π^* are the bonding and anti-bonding orbitals of the π-electron system respectively. The z axis is taken to be perpendicular to the molecular plane. According to Eq. (5), the principal value of g_{zz} is the smallest of all, and is nearly equivalent to the free spin value. This also supports the conclusion that the W radical is the π-electron radical.

As for the other radical, V, which was also trapped at 50°C, its most remarkable difference from the W radical is the loss of the hfs due to the hydrogen. However, the directions of the principal axes of g_1 and $A_1(N)$ are also nearly perpendicular to the molecular plane. Table 3 shows that the values of the Fermi term and the s character of the odd electron orbital on the nitrogen are smaller than those of the σ-electron radical at room temperature. Thus, it seems most probable that the V radical is also a π-electron radical formed by the saturation of the double bond as follows;



$${}^-OOC\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}N\text{-}O\cdot + R''\text{-}R' \longrightarrow {}^-OOC\text{-}\underset{\displaystyle R''}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}\text{-}\underset{\displaystyle R'}{\underset{|}{N}}\text{-}O\cdot$$

Since no hyperfine coupling except for that of the nitrogen was observed, the R′ group probably does not contain the coupling nuclei. The odd electron density on the nitrogen and the magnitude of the Fermi term due to the nitrogen are smaller than

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[8] O. H. Griffith, D. W. Cornell and H. M. McConnell, *J. Chem. Phys.*, **43**, 2909 (1965).

[9] J. G. Baird and J. R. Thomas, *ibid.*, **35**, 1507 (1961).

[10] H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960).

[11] J. R. Rowlands, *Mol. Phys.*, **5**, 565 (1962).

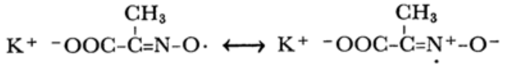
those of the π-electron radical W (see Table 3). This suggests that the delocalization may take place in the π-electron system of the R–N–O fraction. The structure and origin of R′ and R″ can not be clarified on the basis of this experiment.

Free Radicals Trapped in Irradiated Potassium 1-Oximinopropionate

The Features of the ESR Spectra. When a single crystal of potssium 1-oximinopropionate was irradiated at room temperature, two kinds of ESR spectra, KR and KH, were obtained. Each spectrum showed two sets of lines due to the radicals occupying the two different crystal sites when the external magnetic field was in the XY and YZ planes, while it showed one set of lines in the ZX plane. This shows that the symmetry of this crystal is monoclinic and that the plane of symmetry is the ZX plane.

After heating at 50°C for a week, one of the two spectra, KR, vanished and instead a new spectrum KH′ was obtained, while the other radical KH, remained unchanged. The first gave the hfs due to one nitrogen, N_{KR}, only; the second and the third had the same hyperfine tensor, but with different orientations. The latter two had the hfs due to one nitrogen, N_{KH}, and one hydrogen, H_{KH}; this changed to that due to one nitrogen and one deuterium when a deuterated crystal was used.

The Radicals Trapped at Room Temperature and 50°C. The hyperfine and g tensors were determined by the same procedure as was used for the sodium salt. In the KR radical, the principal values of the g tensor are 2.0022 ± 0.0003, 2.0065 ± 0.0004, and 2.0076 ± 0.0002, while those of the nitrogen hyperfine tensors are 43.6 ± 0.2, 24.4 ± 0.6, and 23.6 ± 0.6G. The magnitude of the Fermi term, A_f, the s character, S, and the odd electron density, ρ_N, are listed in Table 3. It is obvious from these data that the KR radical has an electronic structure similar to that of the R radical of the sodium salt; *i. e.*, the σ-electron radical,



$$K^+\ {}^-OOC\text{-}\overset{CH_3}{\overset{|}{C}}{=}N\text{-}O\cdot \longleftrightarrow K^+\ {}^-OOC\text{-}\overset{CH_3}{\overset{|}{C}}{=}\underset{\cdot}{N}^+\text{-}O^-$$

Similar relations are also satisfied for the angles between the principal axes. The bond angle ∠CNO is 142° in this case. The only difference from the R radical is the loss of the observable hydrogen hfs.

In the KH radical, the principal values of the g tensor are 2.0017 ± 0.004, 2.0054 ± 0.003, and 2.0097 ± 0.0003, while those of the nitrogen hyperfine tensor are 31.6 ± 1.5, 11.3 ± 1.8 and 6.3 ± 1.9G. Those of the KH′ radical are the same as those of the KH radical within the limits of experimental accuracy except for the directions of the principal axes. This seems to reflect the fact that the KH and KH′ radicals have the same structure but different orientations. The principal values and the magnitudes of A_f, S, and ρ_N indicate that the KH and KH′ radicals have an electronic structure similar to that of the W radical; they may also be the π-electron radicals formed by the addition of a water molecule to the C=N double bond. Thus, it was found that the trapped radicals are the same for both sodium and potassium salts except for the hfs due to the environment hydrogen.

Radical Pairs

When single crystals of sodium salt were irradiated at −196°C, weak extra absorption lines appeared besides those of the L radical, as is shown in Fig. 5. These lines consist of the two groups of lines which are symmetric with respect to the center of the spectrum of the L radical. The separation of these two groups varies from nearly 150G to −135G in the ac plane; it is at a maximum along the a axis. Each group has a hfs of five equally spaced lines with the intensities of 1 : 2 : 3 : 2 : 1. The separation of these hyperfine lines is always just a half of the nitrogen hyperfine coupling constant of the L radical for any orientation of the magnetic field. Therefore, it is certain that these extra absorption lines are due to the interacting pair of radicals.[12] Similar pairs have already been reported by Kurita for dimethylglyoxime X-irradiated at 77°K.[13] From the separation of the two groups, the distance between the interacting radicals is estimated to be less than 7.2 Å. Because the crystal structure is not known and

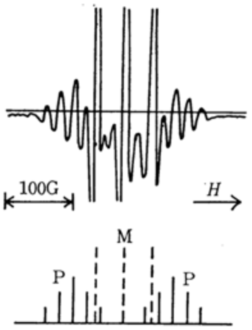


Fig. 5. ESR spectrum of the radical pair of irradiated single crystals of sodium 1-oximinopropionate at −196°C with the magnetic field along the a axis. P and M denote the absorption lines of the radical pair and the monoradical, respectively.

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[12] C. P. Slichter, *Phys. Rev.*, **99**, 479 (1955).

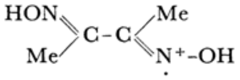
[13] Y. Kurita, *J. Chem. Phys.*, **41**, 3926 (1964).

these absorptions were very weak in contrast with the case of dimethylglyoxime, no complete analysis of this radical pair could be made.

Discussion

The irradiation of organic single crystals at low temperatures has recently been attemped by several workers.13,14) These experiments have shown that radicals at an earlier stage of the reactions in a solid are trapped at low temperatures. In the case of sodium 1-oximinopropionate, however, there is no remarkable difference in the electronic structure between the trapped radical irradiated at −196°C (L radical) and that irradiated at room temperature (R radical). A change in the structure of the radical took place in the higher temperature range, *i. e.*, from room temperature to 50°C.

Miyagawa and Gordy first detected the σ-electron radical in a γ-irradiated single crystal of dimethylglyoxime.4) They assigned it to the cation radical with the following structure:



However, some doubts about the assignment have been offered. Symons15) and Kurita5) have suggested that the neutral radical with the structure (>C=NO·) is reasonable for the trapped radicals in oximes. In this experiment, the trapped radicals, L and R, are shown to be neutral radicals. It seems that the σ-electron radical, L, is the primary radical, since the scission of the O–H bond may be an elementary process.

Though the electronic structures of the R and L radicals are essentially the same, the principal values and axes of the g and A tensors are fairly different: for example, the angles $\angle g_2A_2$ are 5° and 22° for the L and R radicals respectively. These differences are not due to the differences in the thermal motions at different temperatures, since the change in the ESR spectra is not reversible. This seems to indicate that the environments of the radicals are somewhat different at −196°C and at room temperature. It seems to be important that the change in the environment of the radical is detected indirectly by observing the change in the structures of the radicals. Another piece of evidence is the presence of the three hydrogens, H_{La}, H_{Lb}, and H_R, which give appreciable hfs and which are assumed to be hydrogens of the surrounding molecules. The hydrogens interacting at low temperatures, H_{La} and H_{Lb}, are shown to differ from that at room temperature, H_R. This fact reflects the change in the environment. In addition, H_{La} and H_{Lb}, which are not replaced by deuterium, should be methyl hydrogens in origin. If the environment did not change, three hydrogens instead of one would couple equivalently as a result of the rapid internal rotation. This indicates that at least one of the surrounding methyl groups must be replaced by a reaction product. The diamagnetic environment seems to be considerably reactive upon irradiation; *i. e.*, the environment of the radical is changed from that of the molecule of the undamaged crystal. This is contrary to the usual implicit understanding that it does not change appreciably upon irradiation. The change from the σ-electron radical to the π-electron radical in a solid seems to be related to the reactivity of the environment. It should be noticed, however, that the crystal symmetry surrounding the radicals is still conserved in spite of this remarkable change.

After heating at 50°C, two new types of the radicals, V and W, were obtained. It is proposed that they are formed by the addition reaction to the C=N bond of the R radical. The assignment of the V radical is somewhat uncertain since the R′ in the R′–N–O group is unknown, but it is certain, from the reasons described above, that the W radical is the π-electron radical. In addition, crystalline water molecules are seen to be mobile in the crystal at 50°C.*2 This indicates that the addition of a water molecule to the C=N double bond is reasonable. It has been reported that the $HCH(COOH)\dot{C}H(COOH)$ and $RCH(COOH)\dot{C}H(COOH)$ radicals are formed from fumaric acid in single crystals.16,17) The reaction is the addition of a radical or a hydrogen atom to the unsaturated molecule, while the reaction proposed here is the addition of a molecule to the unsaturated radical. This type of reaction in a solid state has never before been reported.

In single crystals, the anisotropic term of the nitrogen hyperfine tensor from which the spin density on the nitrogen 2p orbital can be determined was observed, in addition to the Fermi term, A_f. The evaluated odd electron density on the nitrogen of the W radical (0.43) was found to be nearly the same as that of the R radical (0.44) in spite of the great difference in the structure and in the magnitude of the nitrogen hyperfine coupling constant between the W and R radicals. One

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14) For example, K. Akasaka, S. Ohnishi, T. Suita and I. Nitta, *ibid.*, **40**, 3110 (1964); J. R. Morton, *J. Am. Chem. Soc.*, **86**, 2325 (1964); H. C. Box, H. O. Freund and K. T. Lilga, *J. Chem. Phys.*, **42**, 1471 (1965).

15) M. C. R. Symons, *J. Chem. Soc.*, **1963**, 1189.

*2 When the crystal was heated at 70°C for a week, it lost crystalline water and became fine powder. At 50°C, no appreciable dehydration was observed after a week heating. However, water molecules may be thought to be mobile in the crystal also at this temperature.

16) R. J. Cook, J. R. Rowlands and D. H. Whiffen, *J. Chem. Soc.*, **1963**, 3520.

17) I. Miyagawa and K. Itoh, *Nature,* in press.

of the reasons for this is that the Fermi term, A_f, of the nitrogen 2s orbital is large; the small change in the s character, S, brings about the great change in the magnitude of the Fermi term. The other reason is that the odd electron is localized almost on the nitrogen and oxygen 2p orbitals in both the radicals. It is interesting that the s character of the π-electron radical W is not so small (7%).

The odd electron density on the nitrogen of the σ-electron radical of several oximes is usually about 40%.[5,15] This value is similar to that evaluated in the present experiment. Since the odd electron is in the antibonding orbital composed of the lone-pair orbitals of the nitrogen and oxygen, from the simple π electron approximation the odd electron density on the nitrogen should be larger than that on the oxygen in view of the smaller core attraction of the nitrogen. This does not, however, coincide with the experimental facts. It seems necessary for the odd electron densities on the nitrogen and oxygen to be calculated in detail considering the total electron system of the radical.

The differences between the trapped radicals in the sodium and potassium salts are as follows. The hydrogen hfs could be observed in the σ-electron radicals, R and L, of the sodium salt. However, no hydrogen hfs could be observed in the σ-electron radical, KR, of the potassium salt. Further, only the σ-electron radical, R, appeared in the sodium salt upon irradiation at room temperature, while the π-electron radical, KH, as well as the σ-electron radical, KR, were produced in the potassium salt by irradiation at room temperature. It was thought that these features originate from the difference in the spatial configuration of the molecules in the crystals of these salts.

Recently the ESR studies of a pair of radicals have been carried out with a rigid solution of sodium fluorenone,[18] with a UV-irradiated single crystal of potassium peroxysulfate,[19] and with an X-irradiated single crystal of dimethylglyoxime.[13] In the case of dimethylglyoxime, the electronic dipole-dipole term and the hfs of the two nitrogens of the pairs were successfully analyzed in detail and their locations and reactions in the crystal were investigated.[13] We have previously noticed the anomalous hfs of the pair and determined the sign and magnitude of its singlet-triplet separation.[20] In the case of sodium 1-oximinopropionate, the signal intensity was too weak to be analyzed completely. Though the existence of radical pairs were confirmed, no further information could be obtained. Kashiwagi and Kurita examined many types of oximes extensively, and found that some of them easily give radical pairs by X- or γ-irradiation, but their yields differ from molecule to molecule[21]; in fact, the formation of radical pairs by X- or γ-irradiation has been detected only in oximes thus far.

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18) N. Hirota and S. I. Weissman, *Mol. Phys.*, **5**, 537(1962); *J. Am. Chem. Soc.*, **86**, 2538 (1964).

19) P. W. Atkins, M. C. R. Symons and P. A. Trevalion, *Proc. Chem. Soc.*, **1963**, 222; S. B. Barnes and M. C. R. Symons, *J. Chem. Soc.*, **1966A**, 66.

20) H. Hayashi, K. Itoh and S. Nagakura, This Bulletin, **39**, 199 (1966).

21) M. Kashiwagi and Y. Kurita, *J. Phys. Soc. Japan*, **21**, 558 (1966); Y. Kurita and M. Kashiwagi, *J. Chem. Phys.*, **44**, 1727 (1966).