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Electron Spin Resonance Study of Radicals Formed by Abstracting Hydrogen from Amides*[1]

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Electron spin resonance (ESR) studies were made on various radicals formed from formamide, acetamide, *N*-methylformamide, *N*-methylacetamide, *N*,*N*-dimethylformamide and propionamide by hydrogen abstraction with hydroxyl radicals produced by the reaction of hydrogen peroxide and titanium trichloride in aqueous solution, using a rapid flow technique. In each case, except for formamide, various π-electron radicals were found. For formamide, *N*-methylformamide, and *N*,*N*-dimethylformamide, carbamoyl and its methyl substituted σ electron radicals were detected. The *g* factor of the σ electron radical is qualitatively discussed.

It is well known that acyl type radicals, thought to be σ electron radicals, are formed as intermediate species in radical reactions of aldehydes or formamides.[1] In the reaction of aldehydes with a hydroxyl radical in aqueous solution, the expected acyl type radicals were not detected with electron

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*[1] This work was presented at the Sixth Symposium on ESR Spectroscopy, Kyoto, Oct., 1967.

[1] C. Walling, "Free Radicals in Solutions," John Wiley & Sons, Inc., N. Y. (1957).

spin resonance (ESR) spectroscopy. Buley and Norman[2] have proposed a reaction mechanism, in which the hydrated aldehyde R–CH(OH)$_2$ behaves as a reactant.[3] It is expected that acyl radicals will be observed when formamides, which barely exist in the form of hydrates NRR′–CH(OH)$_2$ in aqueous solution, react with a hydroxyl radical. An ESR study on intermediate radicals in the oxidation of simple amides with hydroxyl radical at room temperature was carried out using a rapid flow technique with a hydrogen peroxide and titanium trichloride redox system in aqueous solution. In each case, except for formamide, various π electron radicals formed by hydrogen abstraction were found, and for formamide and its *N*-methyl derivatives, ESR spectra attributed to acyl type σ electron radicals (carbamoyl radicals, CONRR′) were observed. It is our purpose here to investigate the properties of intermediate radicals, especially carbamoyl radicals. Recently, Livingston and Zeldes[4] reported an ESR study of free radicals formed from ultraviolet irradiation of a solution of an amide containing either hydrogen peroxide or acetone. A comparative discussion with their results is made in the present paper.

Experimental

The ESR spectrometer employed was a JEOL JES-3BSX instrument operating at a nominal frequency of 9.4 GHz with a 100 kHz field modulation with a TE$_{011}$ cylindrical mode cavity. The static magnetic field was generated by a JES electromagnet with a nominal homogeneity of 1×10^{-6}/sample volume. For measurement of the *g* factor and hyperfine couplings, a glass capillary was attached to the sample tube. The capillary was filled with a reference compound, an aqueous solution of potassium peroxylamine disulfonate. The *g* factor and the hyperfine coupling constant of ^{14}N of the reference compound is 2.00559 ± 0.00001 and 13.07 ± 0.05 gauss, respectively. Estimated error limits are ±0.00002 and ±0.1 gauss for measured *g* factors and hyperfine coupling constants, respectively; otherwise probable errors are cited.

The rapid flow system consists of a JES-SM-1 mixing chamber and a JES-LC-01 capillary sample tube for aqueous solutions. The reagent solutions used were: (A) Acidified (0.1 M H_2SO_4) aqueous titanous chloride solution (0.02 M); (B) aqueous hydrogen peroxide (0.2 M). The substrate was added to solution (A) and its concentration varied within the range 0.3—3 M, so as to obtain a sufficiently intense absorption.

Results and Discussion

The results obtained for each amide are presented separately and discussed. Hyperfine couplings are designated by the letter *a* with a superscript to indicate the magnetic nucleus and a subscript only where ambiguity would otherwise result. In the case of σ electron radicals, *g* factors are useful for the identification of radical structures, and are discussed later.

1. Formamide. The ESR spectrum of the radical formed by the reaction of formamide with hydroxyl radical is shown in Fig. 1. Parameters of this radical are summarized in Table 1. It has a characteristic *g* factor smaller than that of the free spin (2.00232), like vinyl ($g=2.00220$)[5] and formyl ($g=2.0009$)[6] σ electron radicals. In general, *g* factors of π electron radicals are greater than 2.00232.[7]

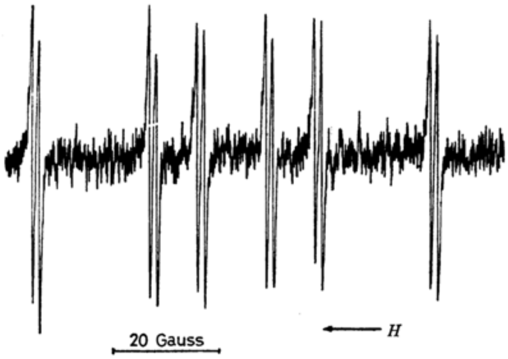

Fig. 1. The ESR spectrum of the radical obtained from formamide.

TABLE 1. ESR PARAMETERS OF THE RADICAL[a] RESULTING FROM HYDROGEN ABSTRACTION FROM FORMAMIDE

	This work	Livingston and Zeldes[b]	Smith and Wood[c]
g	2.00167	2.00155	2.0016
a^{N}[d]	21.8	21.69	21.65
$a^{\mathrm{H}}_{\mathrm{NH},t}$[d]	30.8	30.41	30.55
$a^{\mathrm{H}}_{\mathrm{NH},c}$[d]	1.3	1.27	1.22

a) This radical is assigned to carbamoyl radical (See text). b) Ref. 4. c) Ref. 9. d) In unit of gauss.

Therfore the radical obtained from formamide is

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[2] A. L. Buley and R. O. C. Norman, *Proc. Chem. Soc.*, **1964**, 225.

[3] Aldehydes have been found not to give ESR signals due to acyl radicals even in non-aqueous systems (probably because of their high reactivities). H. Zeldes and R. Livingston, *J. Chem. Phys.*, **47**, 1465 (1967).

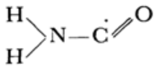
[4] R. Livingston and H. Zeldes, *ibid.*, **47**, 4173 (1967).

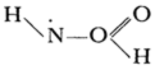
[5] R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

[6] F. J. Adrian, E. L. Cochran and V. A. Bowers, *ibid.*, **36**, 1661 (1962).

[7] a) H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957); b) A. J. Stone, *Mol. Phys.*, **7**, 311 (1963).

expected to be a σ electron radical. Possible structures for the σ electron radical with two nonequivalent protons and one nitrogen nucleus formed from formamide is I, II or III.


I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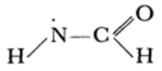
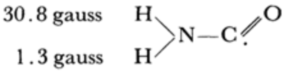

III

As shown later, σ electron radicals which have *g* factors and ^{14}N couplings with values approximately the same as those in Table 1 are formed from *N*-methylformamide and *N,N*-dimethylformamide. From the former, methylcarbamoyl radical (derivative of I) and the radical formed by N–H hydrogen abstraction (derivative of II or III) are possible. The only σ electron radical possible by abstracting hydrogen from *N,N*-dimethylformamide is dimethylcarbamoyl radical (dimethyl derivative of I), which shows that the σ electron radical formed from formamide should be the carbamoyl radical (I). This assignment of the radical formed from formamide is consistent with that of Livingston and Zeldes,[4] who have concluded that a hydroxyl radical formed through UV irradiation abstracts hydrogen bonded to the carbon atom of formamide resulting in a "non –π" radical. This identification also coincides with the theoretical conclusion of the present authors.[8]

On the other hand, Smith and Wood[9] perfomed an experiment similar to the present one and remarked that the radical of Table 1 is HCO$\dot{N}$H, formed by abstraction of hydrogen bonded to nitrogen. However, both experimental[4] and theoretical[8] evidence, together with the discussion given above, show that the radical of Table 1 is a carbamoyl σ electron radical. Referring to the calculated results,[8] the proton splitting constants are assigned as



This assignment is reasonable in comparison with those of vinyl[10] and iminoxy[11] radicals.

Fessenden[12] has reported the ^{13}C coupling constant of the β-carbon in a vinyl radical to be ±8.55 gauss. When the spin density on the 2s atomic orbital is unity, ^{13}C and ^{14}N isotropic splitting constants are calculated to be 1110 gauss and 549 gauss, respectively.[13] The observed ^{14}N isotropic coupling constant of 21.8 gauss in the carbamoyl radical seems somewhat large when compared with the ^{13}C splitting constant of the vinyl radical if both radicals are considered to be planar.[14] The large ^{14}N coupling constant of the carbamoyl may be explained in the following way. When the CNH_2 group in the carbamoyl radical is a shallow pyramid[15] or the amino group is somewhat twisted around the N–C bond from the CNO plane, thus forming a non-planar structure of carbamoyl radical, the odd electron may delocalize into a lone pair orbital on the nitrogen. The odd electron density of the lone pair orbital of the nitrogen will induce a positive spin density at the nitrogen nucleus through spin polarization as well as through the s-nature of the lone pair orbital, resulting in a large isotropic ^{14}N hyperfine coupling constant. From the above, it is thought that the carbamoyl radical does not have a planar structure.

2. *N*-Methylformamide. Radicals formed by the reaction of *N*-methylformamide, $TiCl_3$ and H_2O_2 gave an asymmetric spectrum as shown in Fig. 2a. It is clear that more than one radical

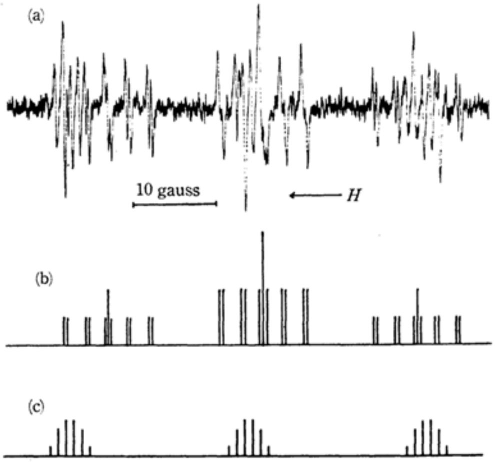


Fig. 2. (a) The ESR spectrum of radicals formed by abstraction of a hydrogen from *N*-methylformamide.
(b) The stick spectrum constructed with parameters of Table 2 for HCONH-$(\dot{C}H_2)$.
(c) The stick spectrum for the methylcarbamoyl radical constructed with parameters listed in Table 3.

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[8] T. Yonezawa, I. Noda and T. Kawamura, This Bulletin, **41**, 766 (1968).

[9] P. Smith and P. B. Wood, *Can. J. Chem.*, **44**, 3085 (1966).

[10] a) E. L. Cochran, F. J. Adrian and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964); b) F. J. Adrian and M. Karplus, *ibid.*, **41**, 56 (1964).

[11] M. Kashiwagi and Y. Kurita, *J. Phys., Soc. Japan*, **21**, 558 (1966).

[12] R. W. Fessenden, *J. Phys., Chem.*, **71**, 74 (1967).

[13] J. R. Morton, *Chem. Revs.*, **64**, 453 (1964).

[14] The calculated isotropic hyperfine coupling constant of ^{14}N in carbamoyl radical with an assumed planar structure is 8.0 gauss, which is small when compared with the observed value. See Ref. 8.

[15] Costain and Dowling concluded from their microwave spectrum study that the CNH_2 group in formamide has a shallow pyramid structure. C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

Table 2. Measured parameters for $HCONH(\dot{C}H_2)$

	This work	Livingston and Zeldes[a)]
g	2.00288	2.00283
$a^H_{CH_2}$[b)]	19.2[c)]	$a^H_{CH_2,1} = 19.05$, $a^H_{CH_2,2} = 18.92$
a^H_{CH}[b)]	5.1	4.83
a^H_{NH}[b)]	0.4	0.32
a^N[b)]	2.6	2.50

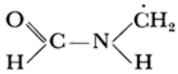
a) Ref. 4. b) In unit of gauss. c) Coupling constants of two protons in the $-\dot{C}H_2$ group are not strictly the same as is seen from the comparison between line shaps of the low-field side doublet in the high-field cluster and the low-field side doublet in the central cluster of Fig. 2a.

Table 3. Parameters of methylcarbamoyl radical (V)

g	2.00182
a^H_{NH}[a)]	2.0
$a^H_{CH_3}$[a)]	1.0
a^N[a)]	22.2

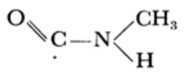
a) In unit of gauss.

is present. This spectrum can be analyzed as two superimposed spectra shown in Figs. 2b and 2c, constructed with the parameters given in Tables 2 and 3. The radical of Table 2 (*i. e.* Fig. 2b) can be assigned to a π electron radical $HCONH(\dot{C}H_2)$. Livingston and Zeldes[4)] have observed essentially the same spectrum as in Fig. 2b during photolysis of a 30% aqueous solution of *N*-methylformamide containing 1% H_2O_2, and identified the radical as $HCONH(\dot{C}H_2)$, with the possible structure



IV

The radical of Table 3 (*i. e.* Fig. 2c), which was not observed in the ESR-photolysis-study of Livingston and Zeldes,[4)] is identified as a methyl carbamoyl σ electron radical with the configuration

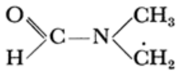


V

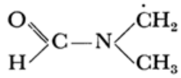
This assignment is based on following results: (1) the g factor of this radical (2.00182) is smaller than the spin-only value (2.00232) and resembles that of the carbamoyl radical formed from formamide (Table 1); (2) the ^{14}N coupling constant is nearly equal to that of the carbamoyl radical: (3) this radical should have a configuration with the NH bond *cis* to the odd electron σ orbital, otherwise the value of a^H_{NH} should be of the same order as $a^H_{NH,t}$= 30.8 gauss of the carbomoyl radical; (4) in the case of σ electron radicals, it is reasonable that the coupling constant of the methyl proton decreases from 30.8 gauss ($a^H_{NH,t}$ of the carbamoyl radical, Table 1) to 1.0 gauss ($a^H_{CH_3}$ of the methylcarbamoyl radical, Table 3) when the hydrogen in the amino group is substituted by a methyl group.

The NMR and IR studies[16)] showed that *N*-methylformamide has its formyl hydrogen *trans* to the NCH_3. It is interesting that the abstraction of formyl hydrogen from *N*-methylformamide by a hydroxyl radical does not change the conformation of the skelton of O=C–N–C.

3. *N,N*-Dimethylformamide. Radicals formed from the reaction between *N,N*-dimethylformamide and hydroxyl radicals prepared by the redox reaction of $TiCl_3$ and H_2O_2 give a very complex ESR spectrum, as shown in Fig. 3a. The spectrum consists of three clusters of lines. All three clusters of lines were measured in considerable detail, and it was clear that three radical species resulting from abstraction of a hydrogen atom from a methyl or formyl groups were present. The spectrum of Fig. 3a consists of three spectra, Figs. 3b, 3c and 3d, constructed with the parameters listed in Tables 4, 5 and 6, respectively. The radicals in Table 4 and 5 (*i. e.* Figs. 3b and 3c) are easily identified as geometrically isomeric π radicals, $HCON(\dot{C}H_3)$-$(\dot{C}H_2)$, formed by the abstraction of methyl hydrogen. A comparison of the parameters of Tables 2, 4 and 5 suggests that the radical of Table 5 has the same coformation as the radical from *N*-methylformamide. Assuming that $HCONH(\dot{C}H_2)$ has the conformation of IV in the preceding section, the radicals of Tables 4 and 5 may have the conformations VI and VII shown below, respectively.

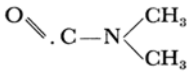


VI



VII

The radical of Table 6 with a small g factor is identified as dimethylcarbamoyl σ electron radical VIII.



VIII

The proton coupling constant of 0.7 gauss is assigned to the protons of the methyl group *trans* to the odd electron orbital in comparison with *N*-methylcarbamoyl radical formed from *N*-methylformamide. The proton coupling of the methyl group *cis* to the odd electron orbital is small and not resolved.

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16) a) V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **32**, 1272 (1960); b) R. L. Jones, *J. Mol. Spectry.*, **2**, 581 (1958) and references cited therein.

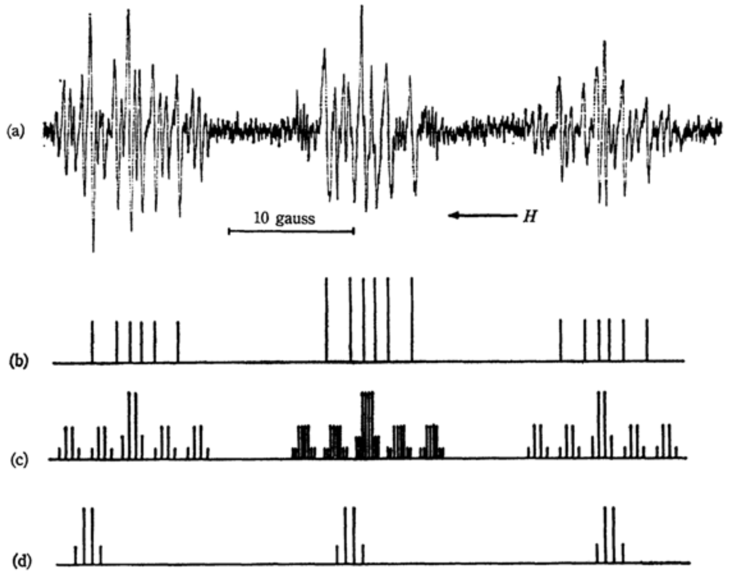

Fig. 3. (a) The ESR spectrum observed during the reaction of *N,N*-dimethylformamide and hydroxyl radical.
(b) The reconstructed spectrum with parameters of Table 4.
(c) The reconstructed spectrum with parameters listed in Table 5.
(d) The stick spectrum constructed with parameters given in Table 6 for dimethylcarbamoyl.

TABLE 4. PARAMETERS FOR THE RADICAL (VI) FORMED BY ABSTRACTING A HYDROGEN FROM METHYL GROUP *cis* TO THE FORMYL HYDROGEN OF *N,N*-DIMETHYLFORMAMIDE

	This work	Livingston and Zeldes[a)]
g	2.0030[b)]	2.00296
$a^{\mathrm{H}}_{\mathrm{CH_2}}$[c)]	18.7[d)]	$a^{\mathrm{H}}_{\mathrm{CH_2,1}} = 18.46$, $a^{\mathrm{H}}_{\mathrm{CH_2,2}} = 18.33$
$a^{\mathrm{H}}_{\mathrm{HC}}$[c)]	3.0[d)]	2.72
$a^{\mathrm{H}}_{\mathrm{CH_3}}$[c)]	~0[d)]	0.32
a^{H}[c)]	1.9[d)]	1.58

a) Parameters for Isomer II of $\mathrm{HCON(CH_3)(\dot{C}H_2)}$ of Livingoston and Zeldes. Ref. 4.
b) Probable erorr: ±0.0001. c) In unit of gauss.
d) Probable error: ±0.3 gauss.

TABLE 5. PARAMETERS FOR THE RADICAL (VII) FORMED BY ABSTRACTING A HYDROGEN FROM $\mathrm{CH_3}$ *TRANS* TO THE FORMYL HYDROGEN OF *N,N*-DIMETHYLFORMAMIDE

	This work	Livingston and Zeldes[a)]
g	2.0029[b)]	2.00284
$a^{\mathrm{H}}_{\mathrm{CH_2,1}}$[c)]	19.0[d)]	18.54
$a^{\mathrm{H}}_{\mathrm{CH_2,2}}$[c)]	18.5[d)]	18.37
$a^{\mathrm{H}}_{\mathrm{CH}}$[c)]	5.2[d)]	4.72
$a^{\mathrm{H}}_{\mathrm{CH_3}}$[c)]	0.5[d)]	0.76
a^{N}[c)]	2.6[d)]	2.25

a) Parameters for isomer I of $\mathrm{HCON(CH_3)(\dot{C}H_2)}$ of Livingston and Zeldes. Ref. 4.
b) Probable error: ±0.0001. c) In unit of gauss.
d) Probable error: ±0.3 gauss.

TABLE 6. PARAMETERS MEASURED FOR *N,N*-DIMETHYLCARBAMOYL RADICAL (VIII)

g	2.0020[a)]
$a^{\mathrm{H}}_{\mathrm{CH_3,t}}$[b)]	0.7[c)]
$a^{\mathrm{H}}_{\mathrm{CH_3,c}}$[b)]	~0[c)]
a^{N}[b)]	20.8[c)]

a) Probable error: ±0.0001. b) In unit of gauss.
c) Probable error: ±0.3 gauss.

4. Acetamide. The radical obtained from acetamide gave a well-resolved spectrum, as Fig. 4. The ESR spectrum of this radical formed by abstraction of a hydrogen atom by OH radical has been reported by Livingston and Zeldes (OH radical prepared by photolysis of $\mathrm{H_2O_2}$)[4)] and by Smith and Wood (OH radical prepared from the redox reaction between $\mathrm{TiCl_3}$ and $\mathrm{H_2O_2}$).[9)] This radical is $\mathrm{\dot{C}H_2CONH_2}$ π electron radical and its parameters are summarised in Table 7.

Two amino-group protons of this radical are not equivalent, as seen in Table 7. It is interesting that the difference between the coupling constants of these two protons are very large relative to their magnitude (about 16% of their mean value). This difference may be interpreted as follows; (1) polarizabilities of two NH σ bonds are not equal mainly because of the difference in NH bond lengths;[17)] thus, the σ–π exchange interaction

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[17)] Two NH bond lengths of formamide are 1.002 Å and 1.014 Å, respectively (Ref. 15).

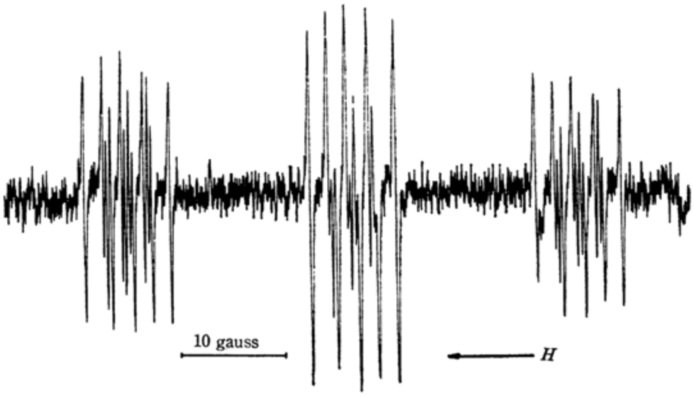

Fig. 4. The ESR spectrum of $\dot{C}H_2CONH_2$ formed by a hydrogen abstruction from acetamide.

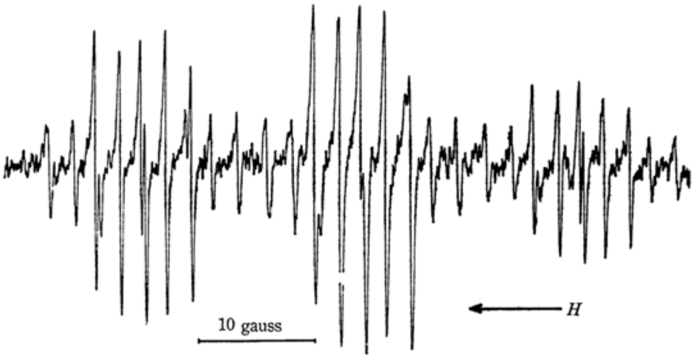

Fig. 5. The ESR spectrum of the radical formed by abstracting hydrogen from *N*-methylacetamide.

induces, at positions of amino-protons, different spin densities and/or (2) amino protons are out of the molecular plane with different angles,[18] then, the odd electron which delocalizes into the two NH σ bonds causes unequal spin densities at the amino-proton positions.

5. *N*-Methylacetamide. Figure 5 shows the spectrum of the radical obtained from *N*-methylacetamide. The ESR parameters are listed in Table 8 along with the parameters reported by Livingston and Zeldes.[4]

The radical was formed by abstraction of a hydrogen atom from a methyl group; there is ambiguity as to which methyl group lost the hydrogen, the choices are $OC(CH_3)NH(\dot{C}H_2)$ and $OC(\dot{C}H_2)NH(CH_3)$. A comparison of parameters of Table 8 with those for π electron radicals from methyl substituted formamides (Tables 2, 4 and 5) and acetamide (Table 7) gives some preference for $OC(CH_3)NH(\dot{C}H_2)$. Friedman and Shechter[19]

Table 7. Measured parameters for $\dot{C}H_2CONH_2$

	This work	Livingston and Zeldes[a)]	Smith and Wood[b)]
g	2.00304	2.00298	2.0034
$a^H_{CH_2}$ c)	21.5	21.34	21.28
$a^H_{NH_2,1}$ c)	2.6	2.43	2.53
$a^H_{NH_2,2}$ c)	2.2	2.04	1.96
a^N c)	1.8	1.72	1.96

a) Ref. 4. b) Ref. 9. c) In unit of gauss.

Table 8. Parameters measured for the radical formed by abstructing a hydrogen from *N*-methyl group of *N*-methylacetamide

	This work	Livingston and Zeldes[a)]
g	2.00282	2.00277
$a^H_{CH_2}$ b)	19.1	18.89 and 18.95
$a^H_{CH_3}$ b)	4.0	3.85
a^N b)	2.2	2.07
a^H_{NH} b)	~0	~0

a) Ref. 4. b) In unit of gauss.

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[18] In the case of formamide, ∠(H′NC plane) (NCO plane) $=7\pm5°$ and ∠(H″NC plane) (NCO plane) $=12\pm5°$, where H′ and H″ designate proton in the NH_2 group. Ref. 15.

[19] L. Friedman and H. Shechter, *Tetrahedron Letters*, **1961**, 238.

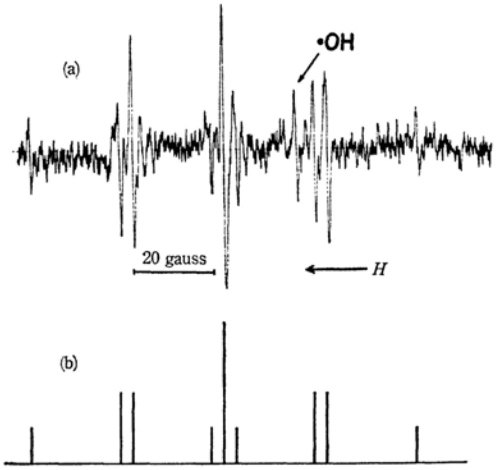

Fig. 6. (a) The ESR spectrum of radicals formed by the reaction of propionamide and hydroxyl radical. The line with an arrow is the signal of remaining hydroxyl radical.
(b) The stick spectrum constructed with parameters of Table 9 for $\dot{C}H_2CH_2$-$CONH_2$.

reported that radical-dimerization of *N*-methylacetamide by *t*-butyl peroxide yields *N,N'*-diacetylethylenediamine (71% yield). This implies that the hydrogen atom in the *N*-methyl group is more easily abstracted than the hydrogen in the acetyl group by radical reactions. Therefore, the radical from *N*-methylacetamide is identified as $OC(CH_3)$-$NH(\dot{C}H_2)$, which agrees with the identification proposed by Livingston and Zeldes.[4)]

6. Propionamide. Radicals formed by the reaction of propionamide with hydroxyl radicals gave the spectrum in Fig. 6a. The spectrum contains three triplets as in Fig. 6b, constructed from the parameters given in Table 9. The radical of Table 9 can be assigned to the radical $\dot{C}H_2CH_2$-$CONH_2$. The remaining lines can not be analyzed because of their low intensity.

TABLE 9. PARAMETERS MEASURED FOR $\dot{C}H_2CH_2CONH_2$

g	2.00275
$a^{\mathrm{H}}_{\mathrm{CH_2}\text{-}}$ a)	22.4
$a^{\mathrm{H}}_{\text{-}\mathrm{CH_2}\text{-}}$ a)	25.6

a) In unit of gauss.

7. *g* Factor of *σ* Electron Radical. Stone[20)] has derived the following expression for one of the diagonal components of the *g* tensor;

$$g^{zz} = g_e + \Delta g^{zz}, \tag{1}$$

where g_e is the free electron *g* factor, 2.00232, and Δg^{zz} is given by

$$\Delta g^{zz} = 2\sum_{n\neq p} \frac{\sum_{k}\sum_{\mu,\nu} C^{(p)}_{k\mu} C^{(n)}_{k\nu} < \chi_{k\mu}|l^z_k|\chi_{k\nu} > \sum_{k'}\sum_{\mu'\nu'} C^{(n)}_{k'\mu'} C^{(p)}_{k'\nu'} < \chi_{k'\mu'}|l^z_{k'}|\chi_{k'\nu'} > \zeta_{k'}}{\varepsilon_p - \varepsilon_n} \tag{2}$$

Here, l_k is the angular momentum about the *k*-th nucleus, ε_p and ε_n are the energies of molecular orbitals $\varphi^{(p)}$ and $\varphi^{(n)}$ and ζ_k is the spin-orbit coupling constant for the *k*th atom. Molecular orbitals $\varphi^{(p)}$ (half-occupied MO) and $\varphi^{(n)}$ (vacant or doubly occupied MOs) are expessed as linear combinations of the *μ*th atomic orbital of the *k*th atom, $\chi_{k\mu}$, as

$$\varphi^{(p)} = \sum_k\sum_\mu C^{(p)}_{k\mu}\chi_{k\mu} \quad \text{and} \quad \varphi^{(n)} = \sum_k\sum_\mu C^{(n)}_{k\mu}\chi_{k\mu}. \tag{3}$$

Similar expressions give the other diagonal components. The *g* factor of a radical in solution is given as the arithmetic mean of the three diagonal elements of the *g* tensor,

$$g = g_e + \Delta g \tag{4}$$

$$\Delta g = \frac{1}{3}(\Delta g^{xx} + \Delta g^{yy} + \Delta g^{zz}). \tag{5}$$

In the case of *σ* electron radicals, MO's with *π* symmetry give large contributions to Δg, since the value of $\varepsilon_p - \varepsilon_n$, which appears in Eq. (2), is small. The odd electron orbital of *σ* radicals are generally localized on one atom. Therefore, the numerator of Eq. (2) often has a positive value, and the sign of Δg of Eq. (5) is, with some exceptions, determined by the energy differences between the half-occupied and lower vacant orbitals, and between the half-occupied and higher doubly occupied orbitals. When the former is smaller than the latter, Δg becomes negative and *vice versa*. Therefore it is expected that for the *σ* electron radical, which has an odd electron localized mainly on the less electronegative atom in that radical and has a higher half-occupied orbital energy, the *g* factor is expected to be smaller than the spin-only value (2.00232). Experimental *g* factors of such *σ* electron radicals as discussed above are summarized in Table 10. On the other hand, iminoxy radicals have been reported[11,21)] to have *g* factors ranging from 2.005 to 2.008, which are much larger than the free-spin *g* factor. The odd electron of the iminoxy radical is mainly localized on the electronegative atoms (oxygen and nitrogen)

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20) A. J. Stone, *Proc. Roy. Soc.*, **A271**, 424 (1963); *Mol. Phys.*, **7**, 311 (1963).

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

Table 10. Reported g factors of σ electron radicals which are smaller than or nearly equal to 2.00232

Radical	g Value	Reference
Vinyl radical	2.00220	Fessenden and Schuler[a)]
1-Methyl-1-vinyl radical	2.00222	Fessenden and Schuler[a)]
HCN anion radical	2.0022	Root *et al.*[b)]
Formyl radical	2.0009	Adrian *et al.*[c)]
2-Pyridyl radical	2.001	Bower *et al.*[d)]
Carbamoyl radical	2.00167	This work
Methylcarbamoyl radical	2.00182	This work
Dimethylcarbamoyl radical	2.0020	This work

a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
b) K. D. J. Root, M. C. R. Symons and B. C. Weatherley, *Mol. Phys.*, **11**, 161 (1966).
c) F. J. Adrian, E. L. Cochran and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962).
d) H. J. Bower, J. A. McRae and M. C. R. Symons, *Chem. Commun.*, **1967**, 542.

of the radical, and the energy level of the odd electron orbital is expected to be low.

Although the above discussions are highly qualitative, they are sometimes useful for the identification of σ electron radicals. It is noteworthy that the substitution of a methyl group into vinyl and carbamoyl radicals enlarges their g factors, as seen in Table 10. Substitution of a methyl group into these radicals elevates energy levels of π orbitals. On the other hand, the energy level of the odd electron σ orbital might be scarcely affected by a methyl substitution. The energy difference between the vacant π and the half-occupied σ orbitals of methyl substituted carbamoyl (or vinyl) radical is larger than that of the carbamoyl (or vinyl) radical. Differences between orbital energies of the half-occupied σ and doubly occupied π orbitals of methyl substituted carbamoyl (or vinyl) radicals are smaller than those of carbamoyl (or vinyl) radical. Both effects enlarge g factors of methyl substituted carbamoyl and vinyl radicals. These explanations for the g factors of carbamoyl, methylcarbamoyl and dimethlcarbamoyl radicals also confirm the present identification of σ electron radicals formed from formamide and its N-methyl and N,N-dimethyl derivatives.