44. *Unstable Intermediates. Part XIV.* The Formyl Radical.*

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An asymmetric doublet with a separation of about 130 gauss is often one component of the electron-spin resonance spectra of irradiated organic compounds. Chemical evidence leading to the postulate that this is due to trapped $\cdot CHO$ radicals is summarised and it is shown that the unusually large isotropic proton hyperfine coupling constant is in accord with expectation for this. The nature of other radicals trapped in the system studied is discussed in the light of their electron-spin resonance spectra.

In an earlier paper,[1] the nature of a radical formed on exposure of $\cdot CH_2\cdot OH$ radicals to ultraviolet radiation and characterised by an asymmetric doublet separated by about 130 gauss,[2] was discussed, and the reaction

$$\cdot CH_2\cdot OH \longrightarrow CH + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

was tentatively proposed. However, this does not explain the remarkably large splitting,[1] and we now suggest that the alternative reaction

$$\cdot CH_2\cdot OH \longrightarrow \cdot CHO + H_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

is more satisfactory since a large isotropic hyperfine splitting from the proton is to be expected for the radical $\cdot CHO$.

A similar doublet to that reported by Alger *et al.*[2] was observed as a component in the electron-spin resonance spectrum of formic acid after exposure to X-radiation,[3] and Miyagawa and Gordy [4] recently found, by substitution with deuterium, that the proton attached to carbon in formic acid is responsible for the hyperfine interaction.

This radical has been characterised by its electronic absorption spectrum,[5,6] and in a rigid matrix by its infrared spectrum,[7] and bond lengths, angles, and force constants have been estimated.

Experimental and Results

Materials.—Hydrogen peroxide (high-test, 86—87% w/w) was kindly supplied by Laporte Chemicals Ltd.

Solid formaldehyde was prepared by heating paraformaldehyde under reduced pressure, the vapour being condensed in a tube immersed in liquid nitrogen.

Other reagents were of the highest grade available and were not further purified.

None of the samples irradiated was degassed and, of those samples which were fluid at room temperature, only formaldehyde solutions formed good glasses when rapidly cooled to 77° K.

Ultraviolet Irradiation.—Three sources were used as indicated in Tables 1 and 2. Source A was a low-pressure mercury-discharge lamp similar to that previously described,[8] the predominant wavelength of the emitted light being 2537 Å. Source B was a Hanovia medium-pressure lamp, the predominant wavelengths being 2537, 3130, and 3650 Å. Source C was a high-pressure mercury arc supplied by G.E.C., the predominant wavelength being 3650 Å, but some light of λ 3130 Å was also present.

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* Part XIII, *J.*, 1961, 12.

[1] Symons, *J.*, 1959, 277.
[2] Alger, Anderson, and Webb, *J. Chem. Phys.*, 1959, **30**, 695.
[3] Gordy, Ard, and Shields, *Proc. Nat. Acad. Sci. U.S.A.*, 1955, **41**, 996.
[4] Miyagawa and Gordy, *J. Amer. Chem. Soc.*, 1960, **83**, 1036.
[5] Herzberg and Ramsay, *Proc. Roy. Soc.*, 1955, *A*, **233**, 34.
[6] Robinson and McCarty, *J. Chem. Phys.*, 1958, **28**, 350.
[7] Ewing, Thompson, and Pimentel, *J. Chem. Phys.*, 1960, **32**, 927.
[8] Symons and Townsend, *J.*, 1959, 263.

Silica tubes containing the samples were immersed in liquid nitrogen, or ethanol at 195° K in a transparent-silica Dewar flask and irradiated with an external lamp for 1—7 hr. After irradiation, samples were quickly transferred to the precooled resonant cavity.

Gamma-irradiation.—Facilities were kindly made available by the Leicester Royal Infirmary; a 100-c ^{60}Co source was used, the total dose being 3×10^6 rad., in 45 hr.

The samples were irradiated at room temperature, and were stored at 195° K immediately after cessation of irradiation.

For electron-spin resonance measurements, the samples were transferred to silica tubes and studied at 195° K.

Electron-spin Resonance Measurements.—Measurements were made on an *X*-band balanced bridge reflection spectrometer with high-frequency alternating magnetic field sampling of the slope of the electron-resonance absorption line. Phase-sensitive detection was used, giving an absolute sensitivity of $5 \times 10^{12}\ \Delta H$ spins, where ΔH is the width of the absorption line.

The microwave generator was a Ferranti klystron of type VA201B. The frequency of oscillation of the klystron was locked to the resonant frequency of the sample cavity by modulating the klystron reflector voltage with a small-amplitude 2 kc./sec. voltage. The off-balance signal obtained at the detector crystal was filtered, amplified, and synchronously rectified, the resulting d.c. signal being applied to the klystron reflector to correct its frequency of oscillation. Transistors were used throughout the frequency locking system because this gave freedom from 50 c./sec. interference.

A rectangular cavity resonating in the HO14 mode was used. It contained a centrally placed loop of wire for high-frequency modulation of the magnetic field applied to the sample. The frequency of this modulation was 100 kc./sec. with a maximum amplitude of 4 gauss.

The d.c. magnetic field was provided by an 8″ pole piece magnet with a 2½″ gap. Power for the magnet was provided by a stabilised power supply, the remaining 100 c./sec. ripple in the output being removed by a choke. The magnet and power unit were manufactured by Newport Instruments Ltd. The stability of the magnetic field was ± 3 in 10^5, the a.c. ripple less than 20 milligauss, and the homogeneity 4 in 10^5.

Magnetic field modulation at 50 c./sec. was provided by subsidiary coils mounted on the main coils of the magnet, the maximum sweep available being 33 gauss.

Slow linear sweep of the field for phase-sensitive detection was obtained by feeding the output from a Miller sweep generator into the control amplifier of the power unit, giving a maximum amplitude of sweep of 800 gauss and maximum time of sweep of 57 min.

The magnetic field was measured by means of a marginal oscillator proton resonance meter. The second harmonic of the frequency of the resonance was measured by means of a T74 frequency meter, manufactured by Telemechanics Ltd. The use of the second harmonic for measurements halved the error due to adjustment of the beats to zero. The accuracy obtained was ± 2 in 10^5. Low-frequency sweep of the proton resonance meter probe was provided by a single-turn loop round it in a plane perpendicular to the d.c. magnetic field. An a.c. current, at a frequency of 50 c./sec., of ½ amp. resulted in a sweep of 1 gauss. As the magnetic field was swept, the signal moved across the screen of an oscilloscope, a second pen on the pen recorder being activated when the resonance reached the centre. The chart paper of the recorder was calibrated by repeating this at several frequencies during a sweep. The value of the magnetic field at an electron resonance absorption could thus be measured. The values of " *g* " were calculated directly, the microwave frequency being measured by means of a Philips wavemeter, type RP4290X. The accuracy realised was $\pm 0{\cdot}0004$ in $2{\cdot}0000$.

The cavity was contained in a bath insulated with polystyrene foam.

For measurements at 77° K the bath was filled with liquid nitrogen, and dry oxygen-free nitrogen was slowly passed through the cavity, to prevent condensation of oxygen and moisture.

A second length of wave-guide, adjacent to the cavity and made of very thin brass supported by a moulded backing of paxolin, served as a heat-break.

The normal wave-guide connected to the heat-break was warmed by a small heater, to prevent condensation of moisture.

For measurements at 195° K the bath was filled with solid carbon dioxide–alcohol.

Results.—Our results on the formyl radical, together with those of other workers, are summarised in Table 1.

Other experiments which might have yielded formyl radicals, but in fact gave rise to other radicals, are listed in Table 2.

TABLE 1.

Reactions which give rise to trapped formyl radicals.

System	Temp. (° K)	Nature of radiation	Details of E.S.R. spectra	Postulated radical	Ref.
MeOH	77	Electrons or *X*-rays	1 : 2 : 1 Triplet (19 gauss)	$\cdot CH_2\cdot OH$	2
MeOH + $\cdot CH_2\cdot OH$	77	2537 Å [a]	Doublet (129 gauss)	$\cdot CHO$	2
MeOH in H_2O (8% v/v)	77	Lamp B	(i) Doublet (132 gauss)	$\cdot CHO$	
			(ii) Quartet (23 gauss)	$\cdot CH_3$	*b*
			(iii) [c]		
MeOH	77	Probably 2200—2300 Å and 2537 Å	(i) Doublet (>120 gauss)	—	*f*
			(ii) Quartet (23 gauss)	$\cdot CH_3$	
MeOH in Ar matrix	4·2	>1450 Å	(i) Doublet	·H atom	
			(ii) Doublet (134·7 gauss)	$\cdot CHO$	*g*
			(iii) [d]	—	
CH_2O (solid)	77	Lamp B	(i) Doublet (≃123 gauss)	$\cdot CHO$	*b*
			(ii) Doublet (17 gauss)	—	
CH_2O (solid)	77	*X*- & γ-Rays	(i) Doublet (125 gauss)	—	*h*
			(ii) Doublet (12 gauss)	$\cdot CHO$	
$CH_2O + H_2O$ (>36% w/v)	77	Lamps A & B	(i) Doublet (132 gauss)	$\cdot CHO$	*b*
or $CH_2O + H_2O + H_2O_2$ (0·2—0·4M)	77	Lamps A, B, & C	(ii) 1 : 3 : 3 : 1 quartet. $g = 2{\cdot}002^2$ (23 gauss)	$\cdot CH_3$	*b*
			(iii) [b]	—	
CH_2O in Ar matrix	4·2	>1450 Å	(i) Doublet	·H atoms	*g*
			(ii) Doublet	$\cdot CHO$	
$H\cdot CO_2H$	77	*X*-Ray	(i) Doublet (12 gauss)	$\cdot CO_2H$	4
			(ii) Doublet (18 gauss)	$H\dot{C}O_2$ or $H\dot{C}(OH)_2$	4
	77	—	New doublet (135 gauss)	$\cdot CHO$	4
$H\cdot CO_2H$ (100%) and H_2O_2 (0·4M)	77	Lamp B	(i) Doublet (133 gauss)	$\cdot CHO$	*b*
			(ii) Line with $g \approx 2{\cdot}002$	—	
HI in CO matrix	4·2	2537 Å	(i) Doublet (134·5 gauss)	$\cdot CHO$	*g*
$C_6H_6 + H_2O + H_2SO_4$	77	U.V.	(i) Doublet (500 gauss)	·H atom	*i*
			(ii) Doublet (~120 gauss)	—	
			(iii) Quartet	$C_6H_6^+$	

[a] 129 Gauss doublet also observed in certain methyl ethers and esters, after ultraviolet bleaching of the radicals formed by high-energy radiation. [b] This work. [c] Another spectrum upon which quartet is superimposed. [d] Weaker incompletely identified resonances. [e] Warmed to 190° K, and recooled to 77° K. [f] Piette, "N.M.R. and E.P.R. Spectroscopy," Pergamon Press, London, 1960, p. 250. [g] Cochran and Adrian, Fifth Internat. Symposium on Free Radicals, Uppsala, Sweden, 1961, Paper 12. [h] Marx and Chachaty, *J. Chim. phys.*, 1961, **58**, 527. [i] Shelimov, Bubnov, Fok, and Voevodsky, *Doklady Akad. Nauk S.S.S.R.*, 1960, **134**, 145; Voevodsky, Fifth Internat. Symposium on Free Radicals, Uppsala, Sweden, 1961, Paper A.1.

TABLE 2.

Other systems studied, that do not give rise to formyl radicals.

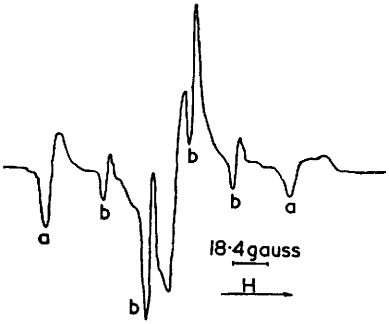
System	Temp. (° K)	Nature of radiation	Details of E.S.R. spectra
Paraformaldehyde $(CH_2O)_3$	77	Lamp B	Very weak signal; width ~18 gauss [a]
	195	γ-Rays	Incompletely resolved doublet (13·6 gauss) with broadening in the wings. $g = 2{\cdot}0038$
Glyoxal monohydrate [approx. $(CHO)_2,H_2O$]	77	Lamp B	Line with pronounced shoulder on low-field side. $g = 2{\cdot}0008$
,, ,,	195	γ-Rays	Incompletely resolved doublet (15·5 gauss). $g = 2{\cdot}0035$
$CH_3\cdot CHO$	77	Lamp B	Single line with two slight shoulders on the high field side; width ~16 gauss. $g = 2{\cdot}0010$
$CH_3\cdot CHO$–H_2O_2 (0·4M)	77	Lamp B	As for $CH_3\cdot CHO$ above [b]
$CH_3\cdot CHO$ in water (20% v/v)	77	Lamp B	(i) Badly resolved quartet (23 gauss) probably due to $\cdot CH_3$. $g = 2{\cdot}0022$ (ii) Single line: $g = 2{\cdot}0015$ (iii) Other small lines
$CH_3\cdot CHO$ in water (20% v/v) + H_2O_2 (0·4M)	77	Lamp B	As for $CH_3\cdot CHO$ in water [c]
$H\cdot CO_2H$	77	Lamp B	Weak single line: $g = 2{\cdot}0010$
$H\cdot CO\cdot NH_2$	77	Lamp B	Weak single line: $g = 2{\cdot}0007$

[a] Width = distance between points of extreme slope. [b] More radicals for same irradiation time, and pink colour. [c] More radicals for same irradiation time, and small lines very small.

Photolysis of Solid Formaldehyde.—The 123 gauss doublet was weak. The radical decayed fairly rapidly, as found by Marx and Chachaty.[9]

Photolysis of Formaldehyde.—When aqueous formaldehyde was irradiated with lamp B at 195° K and studied at the same temperature, no radicals could be detected. At 77° K no radicals could be detected when aqueous formaldehyde was irradiated with lamp C, but irradiation of hydrogen peroxide therein (0·2M) produced a large concentration of radicals. Both lamps A and B produced high concentrations of radicals in aqueous formaldehyde, the presence of hydrogen peroxide only serving to produce about three times as many radicals and not appreciably affecting the relative proportions of the different radicals present. However, the relative proportions of the radicals present were dependent on the time of irradiation and the lamp used. A $\cdot CHO : \cdot CH_3$ ratio of about 18 was obtained by using lamp A for 45 min. on a sample containing hydrogen peroxide whereas use of lamp C on a similar sample for 2 hr. gave a ratio of about 1 : 4. The $\cdot CH_3$ spectrum was always superimposed on a fairly broad line; well-resolved $\cdot CH_3$ spectra with small satellites, one on either side of each component of the quartet, were obtained when the $\cdot CHO : \cdot CH_3$ ratio was low.

A formalin glass, irradiated at 77° K for 2 hr. with lamp B (and giving a $\cdot CHO : \cdot CH_3$ ratio of about 1 : 3), was warmed to 146° K, kept at this temperature for 40 sec., and then recooled to 77° K, whereupon its electron-spin resonance spectrum showed that only a trace of $\cdot CH_3$ radicals remained, whereas the $\cdot CHO$ concentration was practically unchanged. A broad central line was still observed.



First derivative of the electron-spin resonance spectrum obtained from an aqueous formaldehyde glass irradiated for 1½ hours at 77° K with lamp B.

The doublet a is attributed to formyl and the quartet b to methyl radicals.

The Figure shows a typical spectrum obtained from a formalin glass irradiated for 1½ hr. at 77° K with lamp B. The $\cdot CH_3$ spectrum is badly resolved.

DISCUSSION

Identity of the Species.—In this section chemical evidence that the species whose electron-spin resonance spectrum is an asymmetric doublet separated by about 130 gauss is summarised. The following section, which is concerned with structural implications, provides strong supporting evidence.

Probably the most convincing reaction is the addition of hydrogen atoms to carbon monoxide,[10] which has been shown by infrared and ultraviolet spectrophotometry to give rise to formyl radicals.[7] Also the experiments with deuterated methanol [2,11] and formic acid [4] are significant in that they show that the strongly coupled proton is attached to carbon in the parent compounds.

That formyl should be formed from methanol, formaldehyde, and formic acid under the conditions described (Table 1) is in accord with expectation. Probable reaction sequences are:

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[9] Marx and Chachaty, *J. Chim. phys.*, 1961, **58**, 527.

[10] Cochran and Adrian, The Fifth International Symposium on Free Radicals, Uppsala, Sweden, 1961, Paper 12.

[11] Piette, " N.M.R. and E.P.R. Spectroscopy," Pergamon Press, 1960, p. 250.

Methanol

$$CH_3{\cdot}OH + h\nu \longrightarrow H{\cdot} + {\cdot}CH_2{\cdot}OH \qquad (3)$$

$$ {\cdot}H + CH_3{\cdot}OH \longrightarrow H_2 + {\cdot}CH_2{\cdot}OH \qquad (4)$$

$$ {\cdot}CH_2{\cdot}OH + h\nu \longrightarrow {\cdot}H + CH_2O \qquad (5)$$

$$CH_2O + h\nu \longrightarrow {\cdot}H + {\cdot}CHO \qquad (6)$$

Formaldehyde

$$CH_2O + h\nu \longrightarrow {\cdot}H + {\cdot}CHO \qquad (6)$$

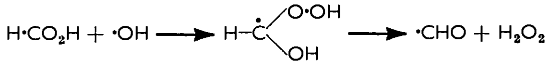
$$\text{or}\left\{\begin{aligned} H_2C(OH)_2 + h\nu \text{ or } {\cdot}OH &\longrightarrow H{\cdot}\dot{C}(OH)_2 \qquad (7)\\ H\dot{C}(OH)_2 &\longrightarrow {\cdot}CHO + H_2O \qquad (8)\end{aligned}\right.$$

Formic acid

$$H{\cdot}CO_2H + h\nu \longrightarrow {\cdot}H + {\cdot}CO_2H \qquad (9)$$

$$ {\cdot}H + H{\cdot}CO_2H \longrightarrow H{\cdot}\dot{C}(OH)_2 \qquad (10)$$

$$H{\cdot}\dot{C}(OH)_2 \longrightarrow {\cdot}CHO + H_2O \qquad (8)$$



$$H{\cdot}CO_2H + {\cdot}OH \longrightarrow H\text{–}\dot{C}\begin{smallmatrix}\diagup O{\cdot}OH\\ \diagdown OH\end{smallmatrix} \longrightarrow {\cdot}CHO + H_2O_2 \qquad (11)$$

Direct extrusion of molecular hydrogen in the photolysis of ${\cdot}CH_2{\cdot}OH$ is excluded by Cochran and Adrian's results.[10] The radical $HC{\cdot}(OH)_2$ is thought to be responsible for the doublet having a coupling constant of about 18 gauss observed by Miyagawa and Gordy.[4] This identification is based on the expectation that reaction (10) should be important, and by comparison of the hyperfine splitting with that found for ${\cdot}CH_2{\cdot}OH$.[12] That this radical should be dehydrated at sufficiently high temperatures is to be expected by comparison with the hydration equilibrium of formaldehyde.

The only reaction which does not seem to be in accord with this assignment is the photolysis of benzene in sulphuric acid.[13] We conclude that some other radical, probably structurally similar to formyl is involved, possibly having a structure of the form $\overset{\cdot}{C}{=}X$ with H attached, $\underset{H\diagup}{{\cdot}C}{=}X$, where X may well be carbon.

Interpretation of the Spectrum Assigned to the Formyl Radical.—In general, it is difficult to interpret the spin-resonance spectra of randomly oriented organic radicals, since magnetic dipole and conformational factors have also to be considered.

Nearly all organic radicals studied have been planar, with the unpaired electron centred partially or wholly in a *p*-orbital on trigonal carbon, and interacting with neighbouring α- or β-protons.

Studies of radicals trapped in specific orientations in single crystals have yielded isotropic and anisotropic hyperfine coupling constants for such protons,[14] and results for a typical radical $CHR_2{\cdot}CHR{\cdot}$ having the unpaired electron strongly localised on trigonal carbon are given in Table 3.

The simplicity of the spectrum under consideration is such that considerable information can be derived despite the random orientation of the radicals responsible. The appearance of one marked shoulder suggests that the radical has approximate axial symmetry, and hence values for $g_{\parallel}$ and $g_{\perp}$ can be estimated corresponding to mid-points between the corresponding points of extreme slope.[15]

Similarly, values for the isotropic (a_{iso}) and anisotropic hyperfine coupling can be estimated from the distances between these points ($a_{\parallel}$ and $a_{\perp}$) and the equation:

$$a_{iso} = \tfrac{1}{3}(2a_{\perp} + a_{\parallel}).$$

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[12] Gibson, Symons, and Townsend, *J.*, 1959, 269.

[13] Shelimov, Bubnov, Fok, and Voevodsky, *Doklady Akad. Nauk. S.S.S.R.*, 1960, **134**, 145; Voevodsky, The Fifth International Symposum on Free Radicals, Uppsala, Sweden, 1961, Paper A.1.

[14] Miyagawa and Gordy, *J. Chem. Phys.*, 1960, **32**, 255; McConnell, Heller, Cole, and Fessenden, *J. Amer. Chem. Soc.*, 1960, **82**, 766; Heller and McConnell, *J. Chem. Phys.*, 1960, **32**, 1535; Atherton and Whiffen, *Mol. Phys.*, 1960, **3**, 1; Pooley and Whiffen, *ibid.*, 1961, **4**, 81.

[15] Kneubühl, *J. Chem. Phys.*, 1960, **33**, 1074.

TABLE 3.

Typical values for hyperfine coupling constants for the hypothetical radical $CHR_2{\cdot}CHR{\cdot}$, where R is any group which does not delocalise the unpaired electron strongly and whose possible hyperfine coupling is ignored.

	Isotropic, gauss (Mc./sec.)	Anisotropic, gauss (Mc./sec.)
α-Hydrogen	−22·5 (−63)	+10 (+28), 0 (0), −10(−28)
β-Hydrogen (free rotation)	+25 (+70)	≏2 (+5), ≏ −0·5 (−1), ≏ −1·5 (−4)
β-Hydrogen [a]	+46·5 (+130)	≏ +3 (+9), ≏ −0·5 (−1), = −2·5 (−8)
β-Hydrogen [b]	+2 (+6)	≏ +2 (+5), ≏ −0·5 (−1), ≏ −1·5 (−4)

[a] CH bond close to a plane at 90° to the nodal plane. [b] CH bond close to the nodal plane.

Results are given in Table 4. It should be stressed that this procedure is only justified if there is axial symmetry. This is not strictly correct here since the low-field side of the narrower component is far sharper than that of the broader component, suggesting that there is a second unresolved shoulder, on the low-field side of the latter component.

TABLE 4.

Parameters derived from the electron-spin resonance spectrum attributed to the formyl radical.

$g_{\parallel}$	$g_{\perp}$	g_{av}	Isotropic H.F.S. gauss (Mc./sec.)	Anisotropic H.F.S. gauss (Mc./sec.)
1·9961	2·0031	2·0008	136 (381)	+8 (+22·4), −4 (−11·2), −4 (−11·2)

It would indeed be surprising to find axial symmetry in the magnetic properties of the formyl radical, which has a bond angle of about 120°.[5] Despite these limitations it is safe to conclude that the average of the three principal g-values for this radical is very close to 2·0008 and that they lie between 2·0031 and 1·9961. Also a_{iso} is close to 136 gauss and the total anisotropy is about 12 gauss.

We consider that these results supply strong additional evidence that the formyl radical is responsible for this spectrum. Comparison with the data of Table 3 shows that the unpaired electron is an orbital which is not even approximately a pure carbon p-level. The large isotropic coupling to one proton means that the unpaired electron must spend about 25% of its time in an s-state on hydrogen, and the small anisotropic coupling shows that the orbital is otherwise well removed from this proton. g_{av}, being less than the free-spin value of 2·0023, indicates that orbital motion is not completely quenched and is that of an electron in a less than half-filled level.

All these conclusions are in accord with expectation for the formyl radical. Since the bond angle is so close to 120° it appears that a good first approximation to the structure of formyl is one in which the carbon has sp^2-hybridisation, the unpaired electron being localised in one such orbital. This structure would explain the small dipolar contribution to the hyperfine splitting, the average distance between the electron and the proton being comparable with that for β-hydrogen in the radical $CHR_2{\cdot}CHR{\cdot}$ (Table 3). However, this arrangement results in a weakening of the bond to oxygen, relative to nitric oxide, and therefore Linnett[16] has surmised that the electronic structure is "intermediate between that in which the CH bond is an electron pair bond and the CO a four-electron one, and that in which the CH is essentially a one-electron bond and the CO a five-electron bond." This prediction is in excellent accord with the electron-spin resonance spectrum assigned to the formyl radical, and, in particular, explains the very large value for the

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[16] Linnett, *Canad. J. Chem.*, 1958, **36**, 24.

isotropic coupling constant. Insofar as there is a one-electron CH bond, when the electron is close to the proton the valence-bond structure $\cdot H[CO]$ is approached, and favoured by the extra stability associated with carbon monoxide. When the electron is close to carbon, the form H^+CO^- is approached. The ion CO^- is isoelectronic with nitric oxide, and hence such a structure will tend to lower the *g*-value below 2·0023.

The Formation of Methyl Radicals.—Assignment of the quartet depicted in the Figure to methyl radicals rests upon the observations that the lines are very narrow, suggesting that the radicals are still tumbling rapidly, that the hyperfine coupling constant is about 23 gauss, and that the intensity ratio is accurately 1 : 3 : 3 : 1. These features are characteristic of methyl radicals.

That methyl radicals in relatively high concentration should result when aqueous formaldehyde is exposed to ultraviolet light, but not from a similar treatment of pure formaldehyde, is curious. The ultraviolet spectrum of the formaldehyde solutions used has a very weak shoulder in the 280 mμ region which is thought to be due to free formaldehyde in low concentration, but there is also an intense absorption band beginning in this region which is thought to be due to the hydrate $CH_2(OH)_2$. One relatively simple route to methyl would then be:

$$CH_2(OH)_2 + h\nu \longrightarrow CH_2 + H_2O_2 \quad \text{. . . . .} \quad (12)$$

$$CH_2 + CH_2(OH)_2 \longrightarrow \cdot CH_3 + \cdot CHO + H_2O \quad \text{. . . . .} \quad (13)$$

There is some precedent for the postulate of direct extrusion of hydrogen peroxide (reaction 12) from the observation that oxygen is similarly formed, almost certainly in one step, when permanganate is photolysed.[17] The reactivity of methylene is such that it would not be expected to be trapped under the conditions used.

This type of reaction does not explain the formation of methyl from methanol. Failure to trap appreciable quantities of $\cdot CH_2\cdot OH$ radicals under these conditions suggests that they absorb strongly in the 2537 Å region and decompose with a high quantum efficiency. Since hydroxyl radicals are known to give $\cdot CH_2\cdot OH$ from methanol under these conditions [12] it is possible that photolysis results in carbon–oxygen bond scission to give methyl, and finally formyl, radicals.

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[17] Klãning and Symons, *J.*, 1959, 3269.