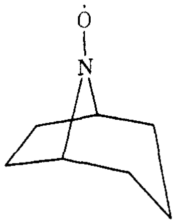
to any change in the overall preexponential factor, A_{epr}. Unfortunately, it proved impossible to measure the equilibrium constant for dimer formation in any solvent other than CF_2Cl_2 and therefore it was not possible to evaluate separately K_1 and k_3 in any other solvent. However, it seems likely that the *primary* cause of the decrease in k_{epr} in the more polar solvents is due to a decrease in the concentration of dimer rather than to any change in k_3. That is, in the more polar solvents (H_2O, alcohol, etc.) the heat of solvation of the nitroxide radicals will be greater than the heat of solvation of the dimer since the polar N–O group will be more exposed. This effect may be counterbalanced to some extent by an entropy factor if strong solvation of the nitroxide radicals results in an increase in the degree of ordering of the solvent molecules. Provided the entropy effect does not override the effect due to the heat of solvation, (*i.e.*, provided the temperature is not too high) the equilibrium constant K_1 should shift so as to favor the free radical as one goes along the solvent series from isopentane to water. Some support for this conclusion comes from measurements of the equilibrium constant for dimer formation for the unhindered nitroxide radical, nortropane-*N*-oxyl (**8**). This radical is stable at room temperature in neutral solution.[30] We have found that the epr signal due to this radical in solution can be reversibly decreased and increased by cooling and warming. This implies that **8** can form a diamagnetic dimer at low temperatures. Since **8** does not decompose, the equilibrium constant could be measured fairly accurately in some solvents. In isopentane, $\Delta H = 7.2$ kcal/mol and $\Delta S = 14.8$ gibbs/mol which give $K_{300^\circ\mathrm{K}} = 10^{-2.0}$ and $K_{200^\circ\mathrm{K}} = 10^{-4.6}$ *M*. In CF_2Cl_2, $\Delta H = 2.9$ kcal/mol and $\Delta S = -0.2$ gibbs/mol which give $K_{300^\circ\mathrm{K}} = 10^{-2.2}$ and $K_{200^\circ\mathrm{K}} = 10^{-3.2}$ *M*. Thus, the free-nitroxide radical is relatively more abundant below room temperature in CF_2Cl_2 than in isopentane. This is so in spite of the large entropy effect operating so as to favor radical formation in isopentane. We attribute the near zero entropy change for the equilibrium in CF_2Cl_2 to a relatively higher degree of ordering of the solvent molecules around the radicals than around the dimer. Unfortunately the equilibrium constant could not be measured for propanol becuase there was no significant dimerization down to −100°. The epr signal due to the radical did decrease at still lower temperatures but it became asymmetric which suggests that **8** may have crystallized out of the propanol. The equilibrium constant could not be measured in water because of the low solubility of **8**, nor in benzene because of the high freezing point of this solvent. In toluene ΔH was found to be ~3.8 kcal/mol but the relatively limited temperature range available precluded the determination of ΔS.



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Electron Spin Resonance Study on Intermediate Free Radicals in the Addition of Thiols to Unsaturated Compounds

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Abstract: Esr spectra of radicals of the type $RSCHX\dot{C}HY$ have been observed in a flow system by running a Ti^{3+}–H_2O_2 redox reaction in the presence of olefinic compounds or propargyl alcohol and thiols. The results show that the thiyl radical adducts observed in the present study have open-chain classical structures. Conformations of the thiyl radical adducts are discussed based on β-proton hyperfine coupling constants.

Thiols add to olefins and acetylenes *via* a free-radical chain mechanism to form sulfides.[1] The postulated reaction mechanism involves a free-radical species RS–A, in which A represents a unit of composition corresponding to that of the olefin or the acetylene employed. The stereospecificity of homolytic thiol addition reactions has been studied and, in some cases, preferential trans addition reactions have been reported.[2–7] To account for the observation[2] that methyl deuteriomercaptan undergoes photoinitiated addition in a stereospecific trans manner to *cis*- and *trans*-2-butenes in the presence of deuterium bromide, sulfur-bridged radicals are proposed as reaction intermediates.[4] The major product from radical addition of methyl mer-

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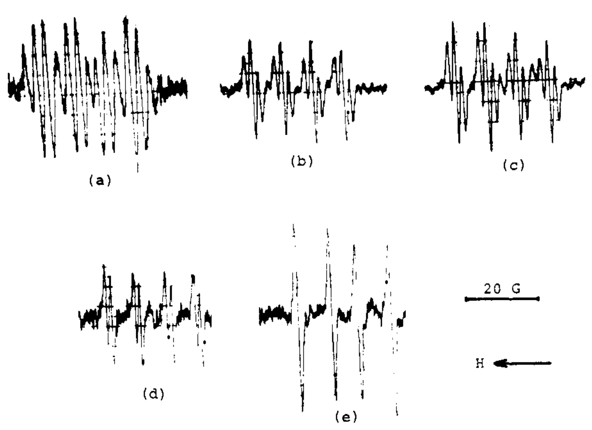


Figure 1. Esr spectra of free radicals: $RS\dot{C}HCH(SR)CH_2OH$: (a) R = CH_3; (b) R = C_2H_5; (c) R = HO_2CH_2, (d) R = i-C_3H_7; (e) R = *tert*-C_4H_9.

captan to 1-chloro-4-*tert*-butylcyclohexene has been found to be *trans*-3-methylmercapto-*trans*-4-chloro-*tert*-butylcyclohexane, the result of diaxial addition.[4] This result has been attributed to the intervention of an unsymmetrically bridged thiyl radical which was said to account for ~88% of the reaction pathway.[4] LeBel and his coworkers[6,7] have extensively studied the stereochemistry of free-radical additions of thiols to substituted cyclohexenes and obtained results which point to the fact that sulfur-bridged intermediates are not involved, at least, in the product-determining steps.

To clarify structures of thiyl radical adducts to unsaturated compounds, we have attempted to detect these intermediates with esr at room temperature (15–25°) by using a rapid flow method developed by Dixon and Norman.[8] Thiyl radicals are generated from the reaction between thiols and hydroxyl radical (or a complex of it) formed from the Ti^{3+}–H_2O_2 redox reaction.

Experimental Section

The flow technique and the esr spectrometer employed are as mentioned earlier.[9] Concentrations of various components in the aqueous solutions are (a) $[H_2O_2]$ = 0.05–0.2 M and [olefin or propargyl alcohol] = 0.005–0.1 M; (b) $[TiCl_3]$ = 0.005–0.01 M, $[H_2SO_4]$ = 0.1 M. Solution b contains a thiol, the concentration of which is 0.1–0.4 M when the solubility of the thiol in water is sufficient, otherwise the thiol is saturated in solution b. The hyperfine coupling constants and the g factors of radicals are determined relative to the total splitting width due to ^{14}N and the g factor of potassium peroxylamine disulfonate, the values of which are assumed to be 26.14 G[10] and 2.00559, respectively. Probable errors in coupling constants and g factors are 0.1 G and 0.0001, respectively. All the measurements are carried at room temperature (15–25°).

Results and Discussion

Propargyl Alcohol. Dixon and Norman[11] have reported that the esr spectrum of the radical $HC{\equiv}C{-}\dot{C}HOH$ is observed when hydroxyl radical is allowed to react with propargyl alcohol.

When titanium trichloride is allowed to react in the esr cavity with hydrogen peroxide in the presence of propargyl alcohol and a thiol such as methyl mercaptan, ethyl mercaptan, thioglycollic acid, isopropyl mercaptan, or *tert*-butyl mercaptan, the esr spectra shown in Figures 1a, 1b, 1c, 1d, or 1e are observed, respectively. Comparison of the spectra in Figure 1 shows that the smallest splittings in these spectra are due to protons in the thiyl group Therefore the observed radical is an adduct of thiyl radical(s) and propargyl alcohol. The g factors of the detected species are high and in the range of 2.0046–2.0049. This shows that the radicals are π electron radicals in which the odd electron is delocalized onto the sulfur atom which has a fairly large L–S coupling constant and lone pairs of electrons. The coupling constants of protons in the thiyl groups of the observed species ($a^{H\gamma}$ in Table I) are large relative to those of thiyl radical adducts to olefinic compounds (*vide infra*), which implies that the odd electron is delocalized onto the sulfur atom. These observed results point to the fact that these species have an α-SR group. Based on the discussions mentioned above and by referring to the results of the study on the reaction of thiyl radicals and acetylenes,[1] the detected species is assigned to a radical having the structure

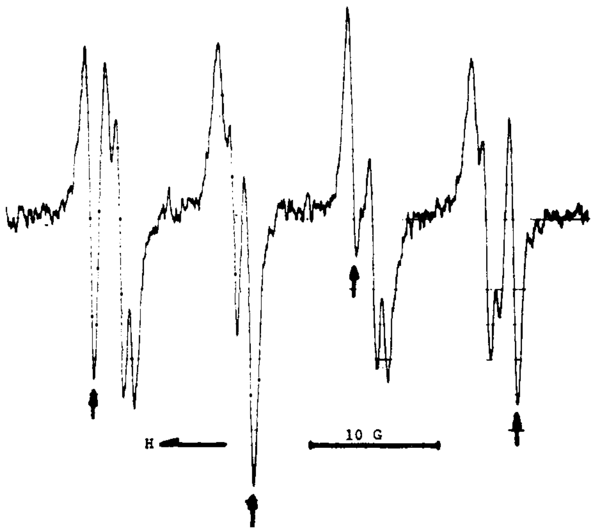
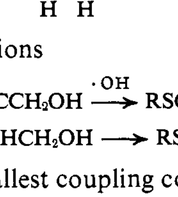


Figure 2. Esr spectrum of free radical $HO_2CCH_2SCH(CO_2H)\dot{C}HCO_2H$.

Table I. Hyperfine Coupling Constants (Gauss) and the g Factor of the Radical $RS\dot{C}HCH(SR)CH_2OH$

R	$a^{H\alpha}$	$a^{H\beta}$	$a^{H\gamma}$ [a]	g
CH_3	(−)16.6	(+)9.0	±2.7	2.0049
C_2H_5	(−)16.6	(+)8.4	±1.9	2.0048
i-C_3H_7	(−)16.5	(+)7.6	±1.6	2.0047
tert-C_4H_9	(−)16.4	(+)9.4		2.0046
HO_2CCH_2	(−)16.8	(+)8.6	±1.8	2.0046

[a] The hyperfine coupling constant due to the protons in the thiyl group attached to the terminal carbon of propargyl alcohol.



$$\begin{array}{cc} RS & SR \\ | & | \\ \cdot C- & CCH_2OH \\ | & | \\ H & H \end{array}$$

formed by the reactions

$$RSH + HC{\equiv}CCH_2OH \xrightarrow{\cdot OH} RSCH{=}CHCH_2OH$$

$$RS\cdot + RSCH{=}CHCH_2OH \longrightarrow RS\dot{C}HCH(SR)CH_2OH$$

The resolved smallest coupling constant is assigned to the protons in the thiyl group attached to the terminal

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(8) W. T. Dixon and R. O. C. Norman, *Proc. Chem. Soc.*, 97 (1963).

(9) T. Yonezawa, I. Noda, and T. Kawamura, *Bull. Chem. Soc. Jap.*, 42, 650 (1969).

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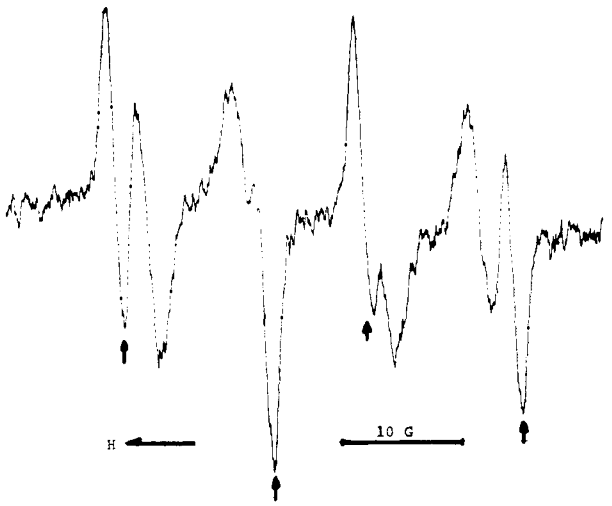

Figure 3. Esr spectrum of free radical $\mathrm{C_2H_5SCH(CO_2H)CHCO_2H}$.

carbon of propargyl alcohol. Observed hyperfine coupling constants of protons and their assignments are shown in Table I together with the observed g factors.

Maleic Acid. When the experiment is run in the presence of maleic acid and thioglycollic acid, the spectrum shown in Figure 2 is observed. The absorptions with arrows are also observed in the experiment without the thiol and are assigned to the radical of 1:1 adduct of hydroxyl radical to maleic acid by referring to the work reported by Fischer.[12] The remaining absorptions correspond to the species $\mathrm{HO_2CCH_2SCH(CO_2H)\dot{C}HCO_2H}$ with $a^{\mathrm{H}\alpha} = (-)\ 20.0$ G (doublet), $a^{\mathrm{H}\beta} = (+)\ 9.0$ G (doublet), the δ proton coupling of ± 0.95 G (triplet), and $g = 2.0033$. The difference in β proton couplings between the present species and the hydroxyl radical adduct to maleic acid as well as the resolved splitting due to protons (δ protons) in the thiyl group confirm the present identification of the radical. Throughout the present study on the addition of thiyl radical to olefinic compounds, the splitting due to protons in the thiyl group is resolved only in the reaction between maleic acid or acrylonitrile and thioglycollic acid.

The esr spectrum shown in Figure 3 is obtained when titanium trichloride is treated with hydrogen peroxide in the presence of ethyl mercaptan and maleic acid. In Figure 3, the absorptions with arrows are due to the hydroxyl radical adduct to maleic acid and the other absorptions are attributed to the species $\mathrm{C_2H_5SCH(CO_2H)\dot{C}HCO_2H}$ with parameters of $a^{\mathrm{H}\alpha} = (-)19.9$ G (doublet), $a^{\mathrm{H}\beta} = (+)8.2$ G (doublet), and $g = 2.0032$, because these parameters resemble those of the radical $\mathrm{HO_2CCH_2SCH(CO_2H)\dot{C}HCO_2H}$.

Isopropyl and *tert*-butylthiyl radicals also add to maleic acid forming $i\text{-}\mathrm{C_3H_7SCH(CO_2H)\dot{C}HCO_2H}$ and $tert\text{-}\mathrm{C_4H_9SCH(CO_2H)\dot{C}HCO_2H}$, which give esr spectra similar to the spectrum in Figure 3. Observed hyperfine coupling constants and the g factor of the radical $\mathrm{RSCH(CO_2H)\dot{C}HCO_2H}$ are summarized in Table II. For comparison, parameters of the hydroxyl radical adduct are also listed in the table.

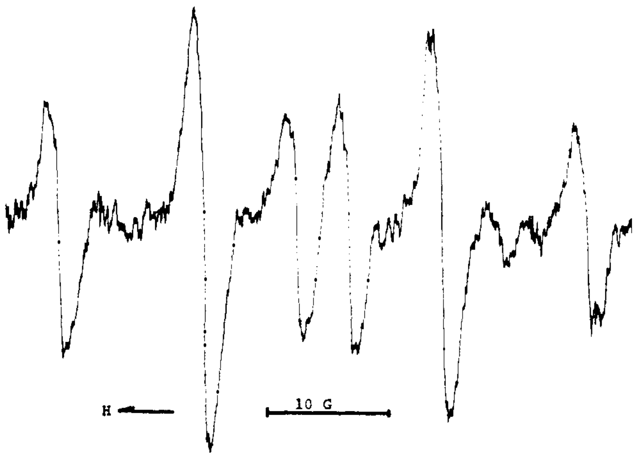

Figure 4. Esr spectrum of free radical $\mathrm{HO_2CCH_2SCH_2CHCO_2H}$.

Table II. Hyperfine Coupling Constants (Gauss) and the g Factor of $\mathrm{XCH(CO_2H)\dot{C}HCO_2H}$

X	$a^{\mathrm{H}\alpha}$	$a^{\mathrm{H}\beta}$	$a^{\mathrm{H}\delta}$ [a]	g
$\mathrm{C_2H_5S}$	(−)19.9	(+)8.2		2.0032
$i\text{-}\mathrm{C_3H_7S}$	(−)20.0	(+)8.0		2.0032
$tert\text{-}\mathrm{C_4H_9S}$	(−)19.9	(+)7.2		2.0032
$\mathrm{HO_2CCH_2S}$	(−)20.0	(+)9.0	±0.95	2.0033
HO	(−)20.9	(+)12.7		2.0033

[a] The hyperfine coupling constant due to protons in the methylene group in the thiyl substituent.

Acrylic Acid. The thiyl radical derived from the thioglycollic acid adds to acrylic acid forming a radical $\mathrm{HO_2CCH_2SCH_2\dot{C}HCO_2H}$ which gives the esr spectrum shown in Figure 4. Observed parameters are $a^{\mathrm{H}\alpha} = (-)19.5$ G (doublet), $a^{\mathrm{H}\beta} = (+)12.0$ G (triplet), and $g = 2.0031$. The radicals formed in the reaction between hydroxyl radical and acrylic acid, $\mathrm{HOCH_2\text{-}\dot{C}HCO_2H}$ and $\mathrm{HO(CH_2CHCO_2H)_{\mathit{n}}CH_2\dot{C}HCO_2H}$, have a β proton coupling constant of 27.58 and 22.06 G, respectively.[12] The present species has a β proton coupling constant far smaller than these coupling constants, which supports the present identification. When the experiment is run in the presence of acrylic acid and a thiol, RSH (ethyl or isopropyl mercaptan), an esr spectrum similar to the spectrum in Figure 4 is observed. The detected species is identified as the radical $\mathrm{RSCH_2\dot{C}HCO_2H}$. The observed hyperfine coupling constants and g factors of these radicals are listed in Table III.

Table III. Observed Hyperfine Coupling Constants (Gauss) and the g Factor of $\mathrm{XCH_2\dot{C}HCO_2H}$

X	$a^{\mathrm{H}\alpha}$	$a^{\mathrm{H}\beta}$	g
$\mathrm{C_2H_5S}$	(−)19.6	(+)11.7	2.0031
$i\text{-}\mathrm{C_3H_7S}$	(−)19.6	(+)11.9	2.0031
$\mathrm{HO_2CCH_2S}$	(−)19.5	(+)12.0	2.0031

Crotonic Acid. Crotonic acid and thioglycollic acid give the spectrum shown in Figure 5. The radical is identified as $\mathrm{HO_2CCH_2SCH(CH_3)\dot{C}HCO_2H}$ with $a^{\mathrm{H}\alpha} = (-)19.4$ G, $a^{\mathrm{H}\beta} = (+)5.6$ G, and $g = 2.0031$. The other thiyl radicals, $\mathrm{C_2H_5S}\cdot$, $i\text{-}\mathrm{C_3H_7S}\cdot$, or $tert\text{-}\mathrm{C_4H_9S}\cdot$, react with crotonic acid to form the radicals $\mathrm{RSCH(CH_3)\dot{C}HCO_2H}$, which give esr spectra of double doublets similar to the spectrum in Figure 5. Hyper-

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(12) H. Fischer, *Z. Naturforsch. A*, **19**, 866 (1964).

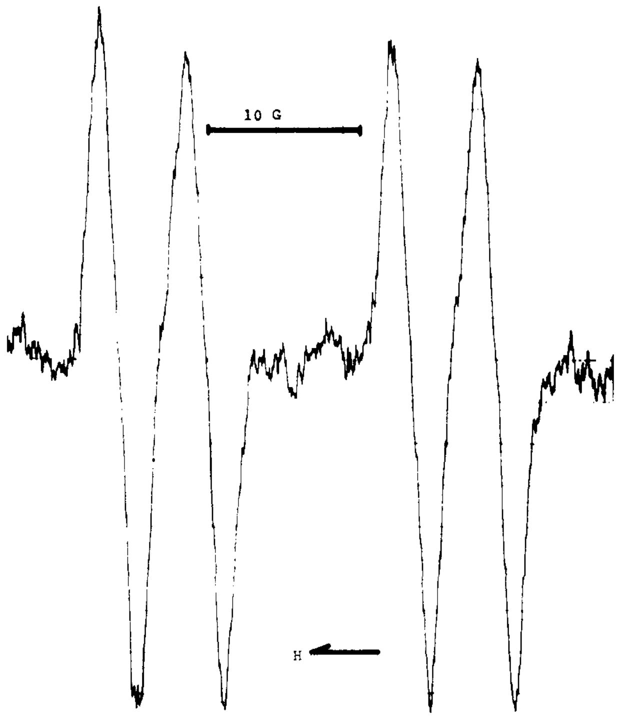


Figure 5. Esr spectrum of free radical $HO_2CCH_2SCH(CH_3)\dot{C}HCO_2H$.

fine coupling constants and the g factor of each radical are tabulated in Table IV. The present identification of the radicals agrees with the work reported by Brown, Jones, and Pinder.[13] They obtained $CH_3SCH(CH_3)CH_2CO_2H$ by the reaction of methyl mercaptan and crotonic acid catalyzed by ascarridole.

Table IV. Observed Hyperfine Coupling Constants (Gauss) and the g Factor of $XCH(CH_3)\dot{C}HCO_2H$

X	$a^{H\alpha}$	$a^{H\beta}$	g
C_2H_5S	(−)19.0	(+)5.5	2.0032
i-C_3H_7S	(−)19.0	(+)5.3	2.0032
tert-C_4H_9S	(−)19.9	(+)5.3	2.0031
HO_2CCH_2S	(−)19.4	(+)5.6	2.0031

Acrylonitrile. Figure 6 shows the esr spectrum obtained during the reaction of thioglycollic acid and acrylonitrile initiated by hydroxyl radical. The spectrum consists of a well-defined ^{14}N triplet of splitting 3.4 G, two sets of 1:2:1 triplets of 14.6 and 0.56 G, and a 1:1 doublet of 20.4 G. The g factor of this radical is 2.0031. The radical can be assigned to $HO_2CCH_2SCH_2\dot{C}HCN$. The reaction of isopropyl mercaptan and acrylonitrile gives the esr spectrum shown in Figure 7, showing that i-$C_3H_7SCH_2\dot{C}HCN$ is formed. Table V summarizes the g factors and hyperfine coupling constants of these radicals together with parameters for the hydroxyl radical adduct.

Table V. The g Factor and Hyperfine Coupling Constants (Gauss) of $XCH_2\dot{C}HCN$

X	$a^{H\alpha}$	$a^{H\beta}$	$a^{H\delta}$ [a]	a^{N}	g
i-C_3H_7S	(−)19.9	(+)14.5		±3.4	2.0028
HO_2CCH_2S	(−)20.4	(+)14.6	±0.56	±3.4	2.0031
HO	(−)20.2	(+)28.6		±3.6	2.0029

[a] The hyperfine coupling constant due to protons in the methylene group in the thiyl substituent.

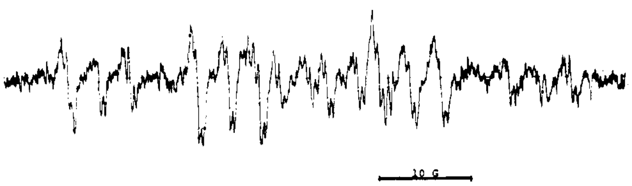


Figure 6. Esr spectrum of free radical $HO_2CCH_2SCH_2\dot{C}HCN$.

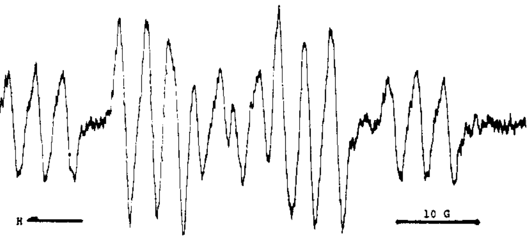
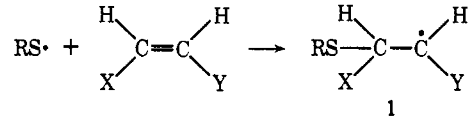


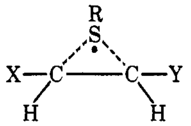
Figure 7. Esr spectrum of free radical i-$C_3H_7SCH_2\dot{C}HCN$.

Structure of Thiyl Radical Adducts to Olefins. The present results show that a thiyl radical adds to olefinic compounds as shown. The symmetrically sulfur-bridged structure 2 and the asymmetrically sulfur-bridged structure 3 have been proposed as structures of the intermediates in the homolytic addition of thiols to butenes and cyclohexenes.[4] The esr parameters of all the thiyl radical adducts in the present esr study show that these adducts have an open-chain classical structure 1. The large difference between hyperfine coupling constants of α and β protons of a thiyl radical adduct is inconsistent with the symmetrically sulfur-bridged structure 2. The g factors of the thiyl radical adducts are nearly equal to those for the corresponding hydroxyl radical adducts, which shows that delocalization of the odd electron onto the sulfur atom is small and that the detected thiyl adducts have not the bridged structure 2 or 3. The α proton coupling constant of a thiyl adduct is nearly equal to that of the corresponding hydroxyl radical adduct, which points to the fact that both species have essentially the same structure around the radical center carbon atom. Thus the detected thiyl radical adducts are concluded to have the open-chain classical structure 1.



1

X = H, CH_3, or COOH
Y = COOH or CN



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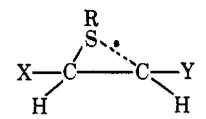

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It should be pointed out that all the radicals which we studied are resonance stabilized by a substituent at-

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(13) R. Brown, W. E. Jones, and A. R. Pinder, *J. Chem. Soc.*, 3315 1951).

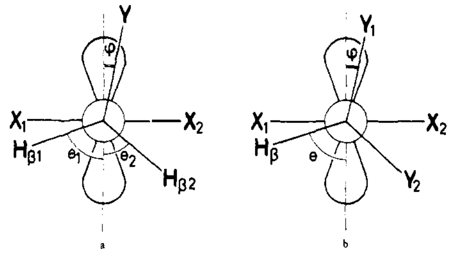

Figure 8. Sterical conformation of (a) $YCH_2\dot{C}X_1X_2$ and (b) $Y_1Y_2CH\dot{C}X_1X_2$.

tached to the radical center carbon atom. Odd electron delocalization onto the sulfur atom is expected to be less important in such cases. Thus the present results do not necessarily exclude the possibility of the sulfur-bridged structure in other cases.[14]

Conformation of Thiyl Radical Adduct. The α proton coupling constants of the thiyl radical adducts to olefins are nearly equal to those of the corresponding radicals generated by $HO\cdot$, $\cdot NH_2$, $\cdot CH_3$, or $\cdot CH_2OH$ addition to olefins.[12,15,16] On the other hand, all the observed hyperfine coupling constants of β protons of thiyl radical adducts are drastically smaller than those of radicals formed by addition of hydroxyl, amino, methyl, or hydroxymethyl radical reported by Fischer and his coworkers.[12,15,16] This implies that the present species exist in the preferred conformation with the C_β—SR bond parallel to the axis of the p orbital containing the odd electron (see Figure 8).

We have estimated the "average" dihedral angle, φ, between the C_β—S bond and the odd electron p_π orbital by referring to the procedure of Fischer.[12] The β proton hyperfine coupling constant, $a^{H\beta}$, is related to the π atomic orbital spin density on the α carbon atom, ρ, and the dihedral angle between the H_β–C_β bond and the odd electron p_π orbital, θ, shown in Figure 8, by the expression

$$a^{H\beta} = B\rho\langle\cos^2\theta\rangle$$

From the above equation and McConnell's equation for the α proton coupling constant

$$a^{H\alpha} = Q\rho$$

we obtain

$$\frac{a^{H\beta}}{a^{H\alpha}} = \frac{B}{Q}\langle\cos^2\theta\rangle \qquad (1)$$

The value of B/Q is estimated to be −2.401 based on the proton hyperfine coupling constants of ethyl radical.[17] The value of the "average" angle φ of the radical with the structure of $XCH_2\dot{C}HY$ can be evaluated by eq 2 which is derived from eq 1.

$$\langle\cos^2\varphi\rangle = -\frac{3}{2} - \frac{2Q}{B}\frac{a^{H\beta}}{a^{H\alpha}} \qquad (2)$$

The average value of φ of the radical with the structure of $XYCH\dot{C}HZ$ cannot be estimated uniquely; the choices are between $\varphi = |60° - \theta|$ and $\varphi = |120° - \theta|$, where θ is evaluated by eq 1. By reference to the values of the "average" angle of the thiyl radical adducts to acrylic acid and acrylonitrile (*vide infra*), we suggest that the sulfur atom of the thiyl radical adduct to crotonic acid or maleic acid is nearly parallel to the axis of the odd electron p_π orbital on the α carbon, that is

$$\varphi = |60° - \theta| \qquad 0° \leqq \theta \leqq 90° \qquad (3)$$

This suggestion is supported by the resolved hyperfine interaction of 0.95 G due to the methylene protons in the thiyl substituent of the radical generated from thioglycollic acid and maleic acid. This type of long-range coupling is suggested[18,19] to be observed when the γ methylene group is eclipsed by the p_π orbital.

The estimated values of the "average" dihedral angle between the C_β—S bond and the axis of the odd electron p orbital, φ, range from 0 to 11° for the thiyl radical adducts to acrylic acid, crotonic acid, and maleic acid, and from 18 to 19° for the thiyl radical adducts to acrylonitrile. These results point to the fact that these species have a predominant low-energy conformation in which the C_β—S bond is nearly eclipsed by the odd electron atomic p orbital at room temperature (15–25°).

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(14) The authors acknowledge the referee and Professor Skell at the Pennsylvania State University who pointed out this possibility.

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