tially in the formation of gel-like solutions at low temperature in DMF and pyridine. This discrepancy is difficult to explain but seems to be related to the basicity and bulkiness of the solvent molecules. Although aggregation occurs in chloroform as revealed by nmr spectroscopy in pure $CDCl_3$, the aggregates in this solvent are not of the same type as observed in pyridine by dielectric measurements.

Side-chain conformation may play an important role in these interactions. Two possible models are proposed on the basis of infrared measurements in the solid state, but there is no evidence at this stage that they are also found in solution.

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Free Radicals from Crotonic Compounds Initiated with Redox Systems

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ABSTRACT: The reactions of crotyl alcohol (CAL), croton aldehyde (CAD), crotonic acid (CAC), and crotonitrile (CNI) with free radicals (R′) from redox reactions ($HO\cdot$, $H_2N\cdot$, and $H_3C\cdot$) have been studied in aqueous solution using esr measurements with a flow system. As a rule two types of radicals were formed from the croton compounds ($C_1—C_2{=}C_3—R$): (A) radicals by addition of R′ to C_3, and (B) radicals by addition of R′ to C_2. The concentration ratio of A to B is a function of R and decreases in the order $CH_2OH > COOH > CN > CHO$. This is interpreted as related to increasing resonance effects of the substituents in the radicals formed which would favor radical B. The concentration ratio of A to B is also affected by the nature of R′ and is found to decrease in the order $H_3C > HO > H_2N$; *i.e.*, the ratio decreases with increasing electron affinity of the attacking radical R′. Some exceptions are found. CAL with $H_3C\cdot$ gives predominantly an allylic type radical by hydrogen abstraction ($CH_3—CH\cdots\dot{C}H\cdots CHOH$). For CAD with $HO\cdot$ only B radicals were found. CAD with $H_2N\cdot$ and $H_3C\cdot$ gave only weak spectra with overlapping lines which could not be assigned to specific radicals. The α-proton coupling constants (a_H^{α}) are 20.0–22.1 G for the various radicals (19.5 G for B radicals of CNI and 16.4 G for B radicals of CAD). The a_H^{β} constants vary more with the nature of the substituents and decrease in the order $HO > H_3C > H_2N$ and $CN > CHO > CH_2OH > COOH$; *i.e.*, they decrease with increased bulkiness of the groups. The $a_{CH_3}{}^{\gamma}$ for the protons decrease in the order $COOH > CHO > CH_2OH > CN$ and $HO \simeq H_3C > H_2N$ which is interpreted as related to the spin density on the γ-CH_3 groups.

1. Introduction

In previous papers from this laboratory,[1-5] the radical polymerization of vinyl esters, butadiene, trimethylolpropane monoallyl ether, and related copolymerization reactions have been studied, using the flow technique developed by Dixon and Norman.[6,7] More recently, we have investigated initiation reactions of allyl[8] and methallyl compounds,[9] and copolymerization reactions of acrylonitrile with several water-soluble monomers[10] using the same method. Similar investigations by Fischer, *et al.*,[11-15] have dealt with various acrylic and methacrylic monomers initiated with several systems. Smith, *et al.*,[16] studied allyl alcohol and Griffiths, et al.,[17] studied vinyl chloride and vinyl fluoride using the flow technique. Two reviews of this field have been published.[18,19]

1,2-Substituted unsaturated compounds have not been homopolymerized but can be copolymerized with other monomers. Not much is known about the free radical mechanisms of the reactions of 1,2-substituted unsaturated compounds, which are complex reactions. Esr measurements using the flow technique have proved very useful for studies of initiation reactions of these monomers. Previously, however, only maleic acid,[7] fumaric acid,[7,12] crotonic acid,[7,12] and crotyl alcohol[17] have been investigated in separate studies. No systematic investigations have been reported.

In this paper, we describe reactions of three types of free radical initiators ($HO\cdot$, $H_2N\cdot$, and $H_3C\cdot$) with four types of crotonic compounds. The reactivity of these monomers to various radicals, the polymerizability of the monomers, the structure and the steric conformation of the transient monomer radicals formed, and the influence of the substituents on coupling constants have been derived from the esr measurements.

2. Experimental Section

The experiments were carried out with an esr instrument equipped with a flow apparatus as previously described.[1,6] The esr spectra of the free radicals were observed during the reaction while the reacting solutions flowed through a flat quartz cell, 0.25 mm thick, inserted in a TE_{102} rectangular resonant cavity of an X-band esr spectrometer (Japan Electron Optics Laboratory, Co., Ltd., Model JES-3B).

Three initiators in aqueous solutions were used: hydroxyl radicals (HO·) from the redox reaction of hydrogen peroxide with titanium trichloride, amino radicals (H_2N·) from the redox reaction of hydroxyl amine with titanium trichloride, and methyl radicals (H_3C·) from the redox reaction of *tert*-butyl hydroperoxide (*t*-BHP) with titanium trichloride.

Two aqueous solutions were used in each case, *i.e.*, one oxidizing solution of H_2O_2, NH_2OH, or $(CH_3)_3COOH$, respectively, containing a monomer (usually about 0.011 mol/l.) and one reducing solution of $TiCl_3$. Both solutions contained either sulfuric acid (to pH 1.4) or ethylenediaminetetraacetic acid (EDTA) and a phosphate buffer (to pH 7). (At low pH values, (NH_2OH, HA) is formed and may take part in the redox reaction, giving $H_3N\cdot^+$ radical ions which could add to the crotonic monomers as stated for the H_2N· radicals. These problems would need a separate study (*cf.* our data in ref 10, p 214).) The two solutions were fed by gravity through rubber tubes, and flowed through the flat cell at a rate of about 4.0 ml/sec. This gives a time lag from mixing to measurements of about 0.015 sec. The free radical spectra were observed during flow and, as a rule, with the reacting solutions at room temperature (22 ± 2°). The magnetic field was calibrated with a proton magnetic resonance signal. The relative concentrations of the radicals were derived from the esr signals (recorded as first derivative curves) and were taken as proportional to the height times the square of the width of the curves.

The following reagents, all of analytical grade, were used in these experiments: 15% titanium trichloride in water, 30% hydrogen peroxide in water, hydroxylammonium chloride, *tert*-butyl hydroperoxide, concentrated sulfuric acid, EDTA, sodium hydroxide, potassium dihydrogen phosphate, and disodium hydrogen phosphate. The monomers, supplied from Schuchardt Co. (West Germany), were of the purest grade commercially available: crotyl alcohol (CAL), crotonic acid (CAC), crotonitrile (CNI), crotonaldehyde (CAD). All monomers were used as received without further treatment.

3. Results

Crotonic acid (CAC) reacted with H_2N· from Ti^{3+}/NH_2OH at pH 1.4 gives two types of radical spectra as shown in Figure 1. The first spectrum is a quartet of doublets of doublets of small triplets with splittings of 25.1, 21.2, 13.9, and 5.1 G which is attributed to radical A of CAC ($C^1H_3\text{-}\dot{C}^2H\text{-}C^3H(NH_2)\text{-}COOH$) produced by the addition of initiator radicals H_2N· to carbon atom 3 substituted with the functional group COOH. The second spectrum is a doublet of doublets of triplets of quartets with splittings of 20.0, 16.7, 3.1, and 1.0 G which is attributed to radical B of CAC ($C^1H_3\text{-}C^2H(NH_2)\text{-}\dot{C}^3H\text{-}COOH$) produced by the addition of initiator radicals H_2N· to carbon atom 2 substituted with a methyl group. The concentration ratio of radicals A to B is about 63:37, and is independent of experimental conditions.

CAC reacted with HO· from Ti^{3+}/H_2O_2 at pH 1.4 gives two types of radicals (Figure 2) as reported by Fischer. The first spectrum is composed of a doublet of quartets of doublets with splittings of 21.9, 25.8, and 16.2 G which is attributed to radical A ($CH_3\text{-}\dot{C}H\text{-}CH(OH)\text{-}COOH$). The second spectrum is a doublet of doublets of quartets with splittings of 20.2, 15.6, and 1.4 G which is attributed to radical B ($CH_3\text{-}CH(OH)\text{-}\dot{C}H\text{-}COOH$). The concentration ratio of radicals A to B is about 70:30. These results are in good agreement with those of Fischer.[12]

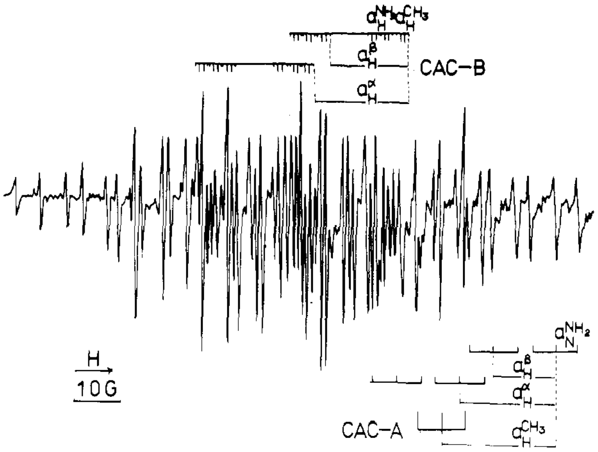


Figure 1. Esr spectrum from crotonic acid (CAC) wih $NH_2OH \cdot HCl\text{–}TiCl_3$: CAC-A, $CH_3\text{–}\dot{C}H\text{–}CH(NH_2)COOH$; CAC-B, $CH_3\text{–}CH(NH_2)\text{–}\dot{C}H\text{–}COOH$; (CAC) = 5.5×10^{-2} mol/l.; ($NH_2OH \cdot HCl$) = 0.25 mol/l.; ($TiCl_3$) = 4.0×10^{-2} mol/l.; (H_2SO_4) = 2.2×10^{-2} mol/l.

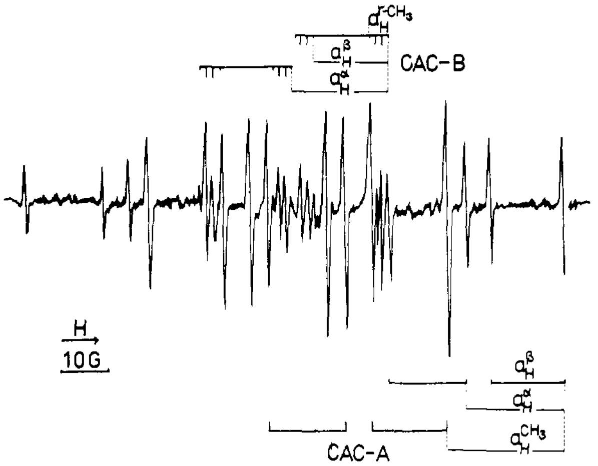


Figure 2. Esr spectrum from crotonic acid (CAC) with $H_2O_2\text{–}TiCl_3$: CAC-A, $CH_3\text{–}\dot{C}H\text{–}CH(OH)COOH$; CAC-B, $CH_3\text{–}CH(OH)\text{–}\dot{C}H\text{–}COOH$; (CAC) = 5.5×10^{-2} mol/l.; (H_2O_2) = 1.1×10^{-2} mol/l.; ($TiCl_3$) = 8.0×10^{-2} mol/l.; (H_2SO_4) = 2.2×10^{-2} mol/l.

CAC reacted with H_3C· from Ti^{3+}/*t*-BHP at pH 1.4 gives two types of radicals as shown in Figure 3. The first spectrum is composed of a doublet of quartets of doublets with splittings of 21.6, 25.6, and 14.6 G which is attributed to radical A ($CH_3\text{-}\dot{C}H\text{-}CH(CH_3)\text{-}COOH$). The second spectrum is doublet of doublets of small septets with splittings of 20.0, 13.0, and 1.2 G which is assigned to radical B ($CH_3\text{-}CH(CH_3)\text{-}\dot{C}H\text{-}COOH$). The concentration ratio of radicals A to B is about 75:25.

Crotyl alcohol (CAL) reacted with H_2N· from Ti^{3+}/NH_2OH at pH 1.4 gives a spectrum as shown in Figure 4. The most intense lines form a doublet of quartets of doublets of triplets with the splittings 21.2, 25.2, 16.1, and 5.1 G. This spectrum can be assigned to radical A ($CH_3\text{-}\dot{C}H\text{-}CH(NH_2)\text{-}CH_2OH$). The additional weak lines could not be satisfactorily analyzed, but may be the spectrum of radical B ($CH_3\text{-}CH(NH_2)\text{-}\dot{C}H\text{-}CH_2OH$) of low intensity.

CAL with HO· from Ti^{3+}/H_2O_2 at pH 1.4 gives very complex spectra (Figure 5). The strongest spectrum is composed of a doublet of quartets of doublets with splittings of 21.6, 25.7, and 17.3 G which is attributed to radical A ($CH_3\text{-}\dot{C}H\text{-}CH(OH)\text{-}CH_2OH$). A weaker spectrum in Figure 5 is a quartet of doublets of small quartets with splittings of 21.8, 16.8, and 0.9 G which is attributed to radical B ($CH_3\text{-}CH(OH)\text{-}\dot{C}H\text{-}CH_2OH$). A still weaker component of the esr spectrum in Figure 5 has too much overlap with other spectra to be assigned to a certain radical species. An

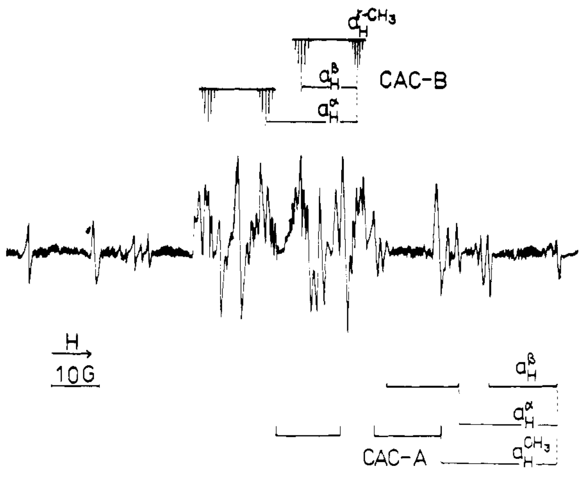


Figure 3. Esr spectrum from crotonic acid (CAC) with $(CH_3)_3COOH$-$TiCl_3$: CAC-A, CH_3-$\dot{C}H$-$CH(CH_3)COOH$; CAC-B, CH_3-$CH(CH_3)$-$\dot{C}H$-$COOH$; (CAC) = 2.75 × 10^{-1} mol/l.; $((CH_3)_3COOH)$ = 0.25 mol/l.; $(TiCl_3)$ = 4.0 × 10^{-3} mol/l.; (H_2SO_4) = 2.2 × 10^{-2} mol/l.

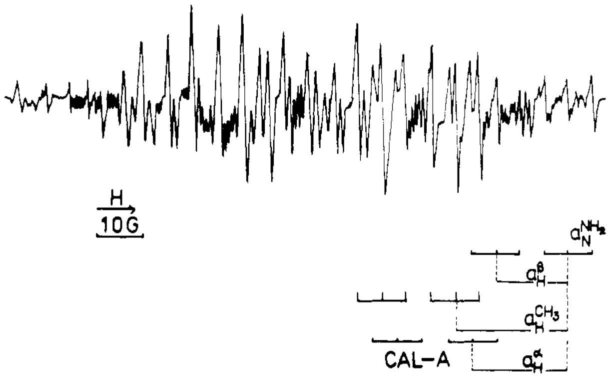


Figure 4. Esr spectrum from crotyl alcohol (CAL) with $NH_2OH \cdot HCl$-$TiCl_3$: CAL-A, CH_3-$\dot{C}H$-$CH(NH_2)CH_2OH$; (CAL) = 2.75 × 10^{-1} mol/l.; $(NH_2OH \cdot HCl)$ = 0.25 mol/l.; $(TiCl_3)$ = 4.0 × 10^{-3} mol/l.; (H_2SO_4) = 2.2 × 10^{-2} mol/l.

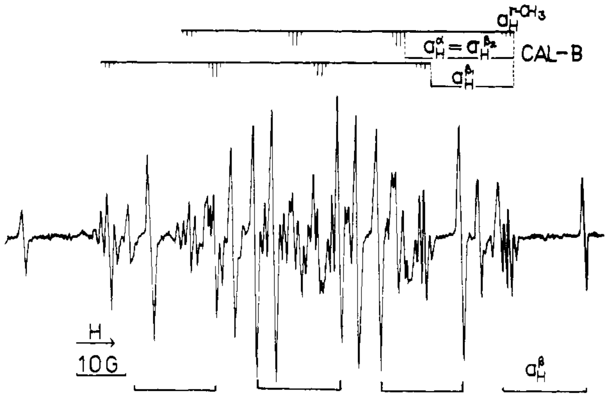


Figure 5. Esr spectrum from crotyl alcohol (CAL) with H_2O_2-$TiCl_3$: CAL-A, CH_3-$\dot{C}H$-$CH(OH)CH_2OH$; CAL-B, CH_3-$CH(OH)$-$\dot{C}HCH_2OH$; (CAL) = 5.5 × 10^{-2} mol/l.; (H_2O_2) = 1.1 × 10^{-2} mol/l.; $(TiCl_3)$ = 8.0 × 10^{-3} mol/l.; (H_2SO_4) = 2.2 × 10^{-2} mol/l.

assignment to allyl radicals of CAL is possible. The concentration ratio of radicals A to B is about 58:42.

CAL reacted with $H_3C\cdot$ from Ti^{3+}/t-BHP at pH 1.4 gives complex overlapping spectra (Figure 6). The dominant spectrum is composed of a quartet of triplets of small doublets with splittings of 15.7, 13.5, and 4.1 G which can be assigned to an allylic type radical AL ($H_3C{-}CH{\cdots}\dot{C}H{\cdots}C(H)OH$) produced by the abstraction of allylic hydrogen from the CH_2OH group of CAL. The less intense lines indicated by arrows in Figure 6 could not be analyzed and assigned. They constitute only a few per cent of the total esr absorption.

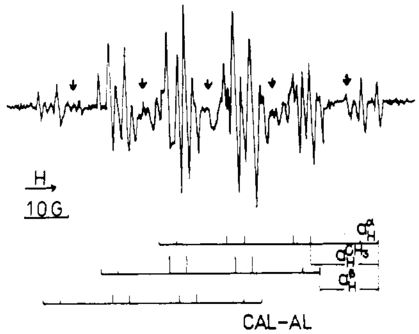


Figure 6. Esr spectrum from crotyl alcohol (CAL) with $(CH_3)_3COOH$-$TiCl_3$: CAL-AL, $H_3C{-}CH{\cdots}CH{\cdots}C(H)OH$; (CAL) = 2.75 × 10^{-1} mol/l., $((CH_3)_3COOH)$ = 2.5 × 10^{-1} mol/l.; $(TiCl_3)$ = 4.0 × 10^{-3} mol/l., (H_2SO_4) = 2.2 × 10^{-2} mol/l.

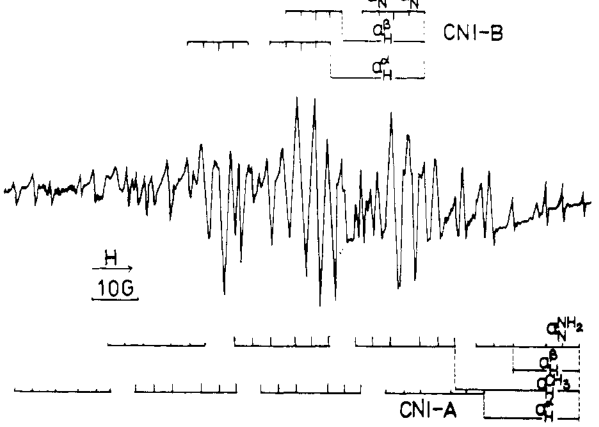


Figure 7. Esr spectrum from crotonitrile (CNI) with $NH_2OH \cdot HCl$-$TiCl_3$: CNI-A, CH_3-$\dot{C}H$-$CH(NH_2)CN$; CNI-B, CH_3-$CH(NH_2)$-$\dot{C}H$-CN; (CNI) = 2.75 × 10^{-1} mol/l.; $(NH_2OH \cdot HCl)$ = 2.5 × 10^{-1} mol/l.; $(TiCl_3)$ = 4.0 × 10^{-3} mol/l.; (H_2SO_4) = 2.2 × 10^{-2} mol/l.

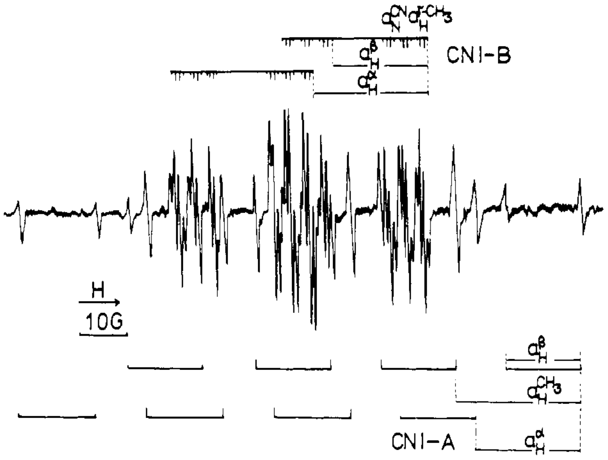


Figure 8. Esr spectrum from crotonitrile (CNI) with H_2O_2-$TiCl_3$: CNI-A, CH_3-$\dot{C}H$-$CH(OH)CN$; CNI-B, CH_3-$CH(OH)$-$\dot{C}H$-CN; (CNI) = 5.5 × 10^{-2} mol/l.; (H_2O_2) = 1.1 × 10^{-2} mol/l.; $(TiCl_3)$ = 8.0 × 10^{-3} mol/l.; (H_2SO_4) = 2.2 × 10^{-2} mol/l.

Crotonitrile (CNI) reacted with $H_2N\cdot$ from Ti^{3+}/NH_2OH

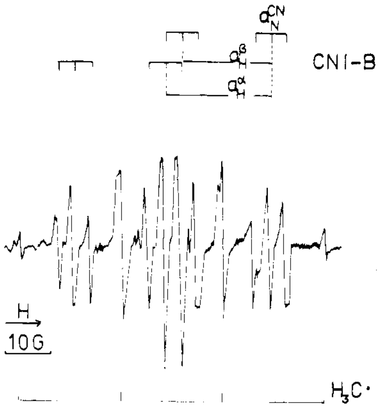


Figure 9. Esr spectrum from crotonitrile (CNI) with $(CH_3)_3COOH$–$TiCl_3$: CNI-B, $CH_3\text{-}CH(CH_3)\text{-}\dot{C}HCN$; (CNI) = 2.75 × 10^{-1} mol/l.; ($(CH_3)_3COOH$) = 2.5 × 10^{-1} mol/l; ($TiCl_3$) = 4.0 × 10^{-3} mol/l.; (H_2SO_4) = 2.2 × 10^{-2} mol/l.

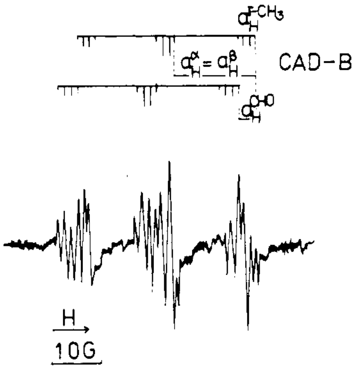


Figure 10. Esr spectrum from crotonaldehyde (CAD) with H_2O_2–$TiCl_3$: CAD-B, $CH_3\text{-}CH(OH)\text{-}\dot{C}HCHO$; (CAD) = 5.5 × 10^{-2} mol/l.; (H_2O_2) = 1.1 × 10^{-2} mol/l.; ($TiCl_3$) = 8.0 × 10^{-3} mol/l.; (H_2SO_4) = 2.2 × 10^{-2} mol/l.

at pH 1.4 gives two types of radical spectra as shown in Figure 7. The first spectrum is a doublet of quartets of doublets of triplets with splittings of 21.1, 25.8, 14.8, and 4.2 G which is attributed to radical A ($CH_3\text{-}\dot{C}H\text{-}CH(NH_2)\text{-}CN$). The second spectrum is a doublet of doublets of quintets with splittings of 20.4, 17.2, and 3.2 G which is attributed to radical B ($CH_3\text{-}CH(NH_2)\text{-}\dot{C}H\text{-}CN$). The concentration of radical A is about 15% of the total.

CNI reacted with HO· from Ti^{3+}/H_2O_2 at pH 1.4 gives two types of radical spectra as shown in Figure 8. The first spectrum is a doublet of quartets of doublets with splittings of 22.1, 26.2, and 15.4 G which is assigned to radical A ($CH_3\text{-}\dot{C}H\text{-}CH(OH)\text{-}CN$). The second spectrum is a doublet of doublets of triplets of small quartets with splittings of 19.5, 23.0, 3.5, and 0.6 G which is assigned to radical B ($CH_3\text{-}CH(OH)\text{-}\dot{C}H\text{-}CN$). The concentration of radical A is about 26% of the total.

CNI reacted with $H_3C\cdot$ from Ti^{3+}/*t*-BHP at pH 1.4 gives a radical spectrum composed of a doublet of doublets of triplets with splittings of 20.0, 23.6, and 3.5 G which is ascribed to radical B ($CH_3\text{-}CH(CH_3)\text{-}\dot{C}H\text{-}CN$) (Figure 9). A methyl radical spectrum ($H_3C\cdot$) is clearly resolved. No spectrum of the expected radical A was detected.

Crotonaldehyde (CAD) reacted with HO· from Ti^{3+}/H_2O_2 at pH 1.4 gives a radical spectrum composed of a triplet of doublets of quartets with splittings of 16.4, 4.1, and 1.2 G which may be assigned to radical B ($CH_3\text{-}CH(OH)\text{-}\dot{C}H\text{-}CHO$) (Figure 10).

CAD reacted with $H_2N\cdot$ and $H_3C\cdot$ at pH 1.4 gives spectra with weak overlapping lines in both cases, which are difficult to assign to specific radicals.

Copolymerization of crotonic acid (CAC) and acrylonitrile (AN) was studied and the reactivity of CAC radicals to AN was found to be almost the same as that of sodium vinyl sulfonate.[10] The reactivity increased to the double when changing pH from 1.4 to 7 as was the case with other acid monomers, *e.g.*, sodium vinyl sulfonate and sodium methallyl sulfonate.[10]

4. Discussion

To summarize the major experimental results reported above, the radical species, the relative radical concentrations, and their coupling constants are all collected in Table I. There are no indications of polymer radicals in the recorded spectra, although rather high monomer concentrations have been used.

Reactivity of Crotyl Compounds to Various Initiating Radicals. Generally, two types of radicals (A and B) could be obtained for crotonic compounds (C^1H_3—$C^2H{=}C^3H$—R) reacted with various initiating radicals. Crotonaldehyde is an exception. The concentration ratio of the two types of radicals depends on the substituents of the crotonic compounds and the type of attacking radicals, as shown in Table II. The concentration ratio of A-type radical decreases with the substituent present in the order CH_2OH > COOH > CN > CHO, which is related to the resonance effect of the substituents. In the case of crotyl alcohol, it is reasonable to assume that the hyperconjugative effect of CH_3 and the lack of resonance effect of the substituent CH_2OH were the reasons that radical A was the major product. When $H_2N\cdot$ was used as initiator radical this effect could not be verified due to overlapping of lines.

Hydrogen abstraction type radicals were expected when HO· attacked crotyl alcohol considering the similarity of this compound to allyl alcohol.[8] It appears to be a general tendency that hydroxyl groups activate the α C–H bond, which facilitates abstraction of hydrogen by an attacking radical. In the case of crotonic acid, radical A was the major product under all experimental conditions studied. This is in contradiction to the general understanding that COOH has stronger resonance effects with an unpaired electron than the hyperconjugative effect of CH_3.[20] As for the attacking radicals, the concentration ratio of type A radicals generally decreases in the order $H_3C\cdot$ > HO· > $H_2N\cdot$. This shows that a nucleophilic radical attacks a carbon atom with an electron-withdrawing substituent easier than a carbon with an electron-donating substituent as CH_3. In the case of CNI, radical B was the major product which may be interpreted as due to the strong resonance effect of the nitrile group. When $H_3C\cdot$ was used as an attacking radical with CNI, only B-type radicals could be found although $H_3C\cdot$ has a nucleophilic property. It has been reported that the rate of addition of radicals with low electron affinity, *e.g.*, $H_3C\cdot$, is a linear function of the delocalized energy of the radicals formed,[21] which may explain the results obtained here. All cases with CAD gave rather unclear spectra. Only B-type radicals could be obtained when the attacking radical was HO·. This may be explained as due to the strong resonance effect of the aldehyde group.

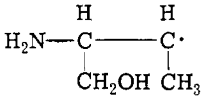
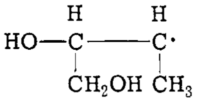
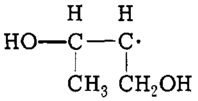
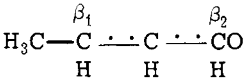
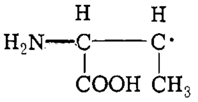
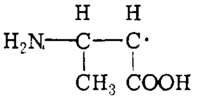
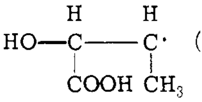
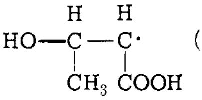
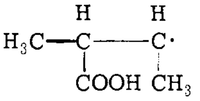
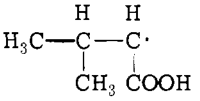
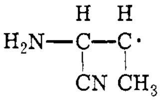
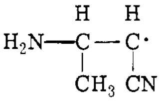
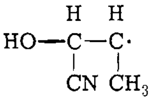
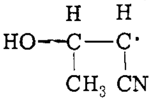
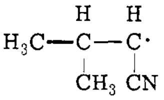
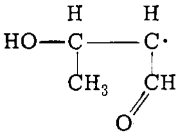
α Protons and α-Methyl Protons. The following discussion is based on the assumption that eq 1 and 2 hold for the coupling constants of α-methyl protons, where ρ is the

$$a_H^{\alpha} = Q_H^{\alpha}\rho \qquad (1)$$

$$a_H^{CH_3} = Q_H^{CH_3}\rho \qquad (2)$$

spin density on the formally trivalent carbon atom. $Q_H^{CH_3}$ is taken as a constant, independent of substitution and

Table I
Radical Structure, Relative Concentrations, and Coupling Constants of Free Radicals Obtained from Crotonic Compounds by Redox Initiation

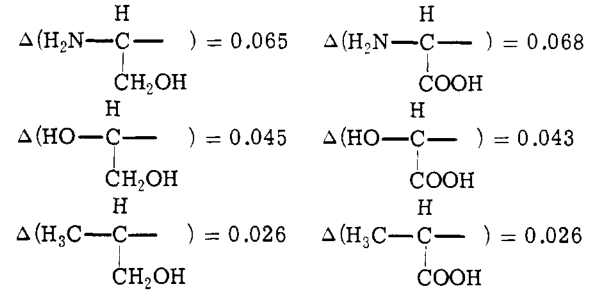
Init radical	Substrate	Radical (rel concn)	a_H^{α}	$a_H^{CH_3}$	$a_H^{\beta_1}$ (init)	$a_H^{\beta_2}$ (allyl)	$a_H^{\gamma\text{-}CH_3}$	$a_H^{NH_2}$	a_N^{CN}	ϕ (ρ)
$H_2N\cdot$	Crotyl alcohol (CAL)	 $H_2N-\underset{CH_2OH}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}\cdot$ (2.64)[a]	21.2	25.2	16.1			5.1		21°54′ (0.860)
$HO\cdot$		 $HO-\underset{CH_2OH}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}\cdot$ (2.43)	21.6	25.7	17.3					24°24′ (0.877)
		 $HO-\underset{CH_3}{\overset{H}{C}}-\underset{CH_2OH}{\overset{H}{C}}\cdot$ (1.82)	21.8		16.8	21.8	0.9			
$H_3C\cdot$		 $H_3C-\underset{H}{\overset{\beta_1}{C}}\cdots\underset{H}{C}\cdots\underset{H}{\overset{\beta_2}{C}}OH$ (1.68)	4.1	15.7	13.5					
$H_2N\cdot$	Crotonic acid (CAC)	 $H_2N-\underset{COOH}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}\cdot$ (1.34)	21.2	25.1	13.9			5.1		13°18′ (0.856)
		 $H_2N-\underset{CH_3}{\overset{H}{C}}-\underset{COOH}{\overset{H}{C}}\cdot$ (0.63)	20.0		16.7		1.0	3.1		
$HO\cdot$		 $HO-\underset{COOH}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}\cdot$ (4.31)	21.9	25.8	16.2					20°54′ (0.881)
		 $HO-\underset{CH_3}{\overset{H}{C}}-\underset{COOH}{\overset{H}{C}}\cdot$ (1.83)	20.2		15.6		1.4			
$H_3C\cdot$		 $H_3C-\underset{COOH}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}\cdot$ (0.78)	21.8	25.6	14.6					15°24′ (0.874)
		 $H_3C-\underset{CH_3}{\overset{H}{C}}-\underset{COOH}{\overset{H}{C}}\cdot$ (0.25)	20.0		13.0		1.2			
$H_2N\cdot$	Crotonitrile (CNI)	 $H_2N-\underset{CN}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}\cdot$ (0.845)	21.1	25.8	14.8			4.2		15°36′ (0.881)
		 $H_2N-\underset{CH_3}{\overset{H}{C}}-\underset{CN}{\overset{H}{C}}\cdot$ (4.96)	20.4		17.2			3.2	3.2	
$HO\cdot$		 $HO-\underset{CN}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}\cdot$ (1.25)	22.1	26.2	15.4					17°18′ (0.894)
		 $HO-\underset{CH_3}{\overset{H}{C}}-\underset{CN}{\overset{H}{C}}\cdot$ (3.64)	19.5		23.0		0.6		3.5	
$H_3C\cdot$		 $H_3C-\underset{CH_3}{\overset{H}{C}}-\underset{CN}{\overset{H}{C}}\cdot$ (0.815)	20.0		23.6				3.5	
$HO\cdot$	Croton aldehyde (CAD)	 $HO-\underset{CH_3}{\overset{H}{C}}-\underset{CH=O}{\overset{H}{C}}\cdot$	16.4		16.4		1.2		(CHO) 4.1	

[a] A small amount of B-type radical may exist.

Table II
Relative Concentration of Radicals A (in % of Total Radical Concentration) of Crotonic Compounds ($R{-}CHR'{-}\dot{C}H{-}CH_3$) with Various Initiator Radicals

Initiator radical (R′)	Substituent (R), % CH_2OH	COOH	CN	CHO
$H_3C\cdot$	98	74	0	
$HO\cdot$	58	70	26	0
$H_2N\cdot$		63	15	

Table III
Δ Values of Various Groups in Radicals from Crotonic Compounds



$$\Delta(\mathrm{H_2N{-}\overset{H}{\underset{CH_2OH}{C}}{-}}) = 0.065 \qquad \Delta(\mathrm{H_2N{-}\overset{H}{\underset{COOH}{C}}{-}}) = 0.068$$

$$\Delta(\mathrm{HO{-}\overset{H}{\underset{CH_2OH}{C}}{-}}) = 0.045 \qquad \Delta(\mathrm{HO{-}\overset{H}{\underset{COOH}{C}}{-}}) = 0.043$$

$$\Delta(\mathrm{H_3C{-}\overset{H}{\underset{CH_2OH}{C}}{-}}) = 0.026 \qquad \Delta(\mathrm{H_3C{-}\overset{H}{\underset{COOH}{C}}{-}}) = 0.026$$

Table IV
β-Coupling Constants of Crotyl Radicals

Init radical (R′)	Substituent (R) −CN	−CHO	$-CH_2OH$	−COOH
(1) A-Type Radicals ($H_3C{-}\dot{C}H{-}CHR'{-}R$)				
$HO\cdot$	15.4**		17.3	16.2
$H_3C\cdot$				14.6
$H_2N\cdot$	14.8		16.1*	13.9
(2) B-Type Radicals ($H_3C{-}CHR'{-}\dot{C}H{-}R$)				
$HO\cdot$	23.0	16.4	16.8	15.6
$H_3C\cdot$	23.6			13.0
$H_2N\cdot$	17.2			16.7*

with a value of 29.3 G assumed, based on experimental results for ethyl, isopropyl, and *tert*-butyl radicals given by Fessenden.[22] The dependence of ρ on substituents is given by Fischer[12] as

$$\rho = \pi(1 - \Delta hi) \tag{3}$$

From eq 2, ρ values for A-type radicals are calculated and shown in Table I. By substituting $\Delta CH_3 = 0.081$ as given by Fischer[12] and the ρ values obtained here into eq 3, Δ values of the various substituents are calculated and shown in Table III.

The values of $a_H{}^{\alpha}$ and $a_H{}^{CH_3}$ increase mainly in the order $H_2N < HO < H_3C$ which follows the reverse order of the electron-withdrawing power of the groups. The α-coupling constants of crotonaldehyde are very small compared with those of other crotonic compounds. For methacrolein, $a_H{}^{CH_3} = 18.0$ G and $\rho = 0.614$ are found which shows that the unpaired electron density of the α carbon is very low in aldehyde compounds.

Steric Conformation of the Observed Radicals. One purpose of this investigation is to study relations between the coupling constants of β-CH_2 protons related to the substituents R. The $a_H{}^{\beta\text{-CH}}$ values for β protons are related to the radical plane ($X_1{-}\dot{C}^{\alpha}{-}X_2$ plane) with $a_H{}^{\beta\text{-H}}$ increasing with increasing ϕ (Figure 11). The angle, ϕ, on the other hand, decreases with increasing bulkiness of the substituents R, X_1, and X_2. Such effects have been nicely shown by Fischer, *et al.*,[14] for acrylic monomer radicals with various initiators. From these arguments, it can be predicted that $a_H{}^{\beta\text{-CH}}$ will decrease if one proceeds along the horizontal rows or the vertical columns of Tables III and IV. This prediction holds within the experimental errors in all rows and columns except for the three values marked by * and **. Those marked by * are exceptionally high and that marked by ** is exceptionally low. A possible interpretation of these deviations is an intramolecular hydrogen bonding as previously proposed[4] in the former cases between the NH_2 group and the substituent on the α carbon and in the latter cases between the HO groups and the substituents on the β carbon.

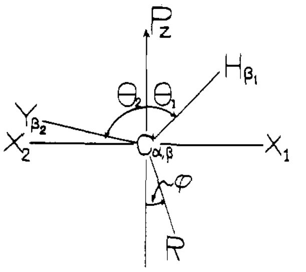


Figure 11. Steric conformation of the free radicals of the type $R{-}C_\beta Y_1Y_2{-}\dot{C}_\alpha X_1X_2$ with the $C_\alpha{-}C_\beta$ bond perpendicular to the paper plane.

The degree of steric hindrance of the monomer radical is clearly related to the value ϕ, which can be calculated from the equation[12]

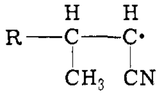
$$a_H{}^{\beta} = \rho B_H{}^{\beta}\,{}^{1}\!/_{4}(3 - 2\cos^2\phi) = \rho B_H{}^{\beta}\,\overline{\cos^2\theta}$$

where ϕ is the angle of free rotation between the projection of the $C^{\alpha}{-}R$ bond and the axis of the $2p_z$ orbital. The angle, ϕ, represents the average position of the substituent, R, projected on a plane perpendicular to the $C_\alpha{-}C_\beta$ bond, as illustrated in Figure 11, $\overline{\cos^2\theta}$ is an average for all angles θ attained, and $B_H{}^{\beta}$ is taken from values reported by Fessenden and Schuler (58.6 G).[22]

The ϕ values of all radicals from crotonic compounds are between 17 and 23° when R is HO. These monomers cannot be homopolymerized but can be copolymerized with less steric hindered monomers like acrylonitrile. The ϕ values of all monomers so far studied that can homopolymerize are higher than 26°,[8] with the exception of vinyl esters, where special effects from hydrogen bonding have been indicated.[4] Therefore, the ϕ values may be used as a measure to predict polymerizability when this property is related to steric hindrance.

γ-CH_3 Splittings and Nitrogen Splittings. The coupling constants of γ-CH_3 protons in crotonic radicals decrease in the order $COOH > CHO > CH_2OH > CN$ for substituents and $HO \simeq H_3C > H_2N$ for initiators as shown in Table V. This indicates that the spin density on the γ-CH_3 groups is decreased by substituents which contribute to the hyperfine splitting.

The value of a_N in the series of



$$\mathrm{R{-}\overset{H}{\underset{CH_3}{C}}{-}\overset{H}{\underset{CN}{C}}\cdot}$$

is dependent upon the nature of R. a_N varies with R in the order $H_3C > HO > H_2N$, *i.e.*, is decreased by electron-withdrawing substituents. The same effects are shown for the

Table V
γ-CH_3 Splittings of Radicals from Crotonic Compounds (R′-$CHCH_3$-$\dot{C}H$-R) (R′ Initiating Radical, R Substituent)

	R			
R′	CN	CH_2OH	CHO	COOH
HO·	0.6	0.9	1.2	1.4
H_3C·	~0	~0		1.2
H_2N·	~0			1.0

Table VI
Nitrogen Splittings of Radicals from Nitrile Monomers

	Monomer		
Init radical	Crotonitrile	Acrylonitrile[a]	Methacrylonitrile[a]
H_3C·	3.5	3.5	3.5
HO·	3.5	3.5	3.4
H_2N·	3.2	3.2	3.2

[a] Corvaja and Fischer, ref 13.

series[23] Me_3C-N(O·)-Ar, where Ar is a para-substituted benzene ring.

5. Synopsis

The effects of three types of free radical initiators (R′ = HO·, H_2N·, or H_3C·) from redox systems have been studied for four types of crotonic compounds (alcohol, aldehyde, acid, and nitrile). The reactivity of these monomers to the various initiator radicals, the polymerizability of the monomers, and the structure and the steric conformation of the transient monomer radicals formed have been derived from information of coupling constants of substituents and radical concentrations, measured by esr in solution, using a flow system.

Generally, two types of radicals (A and B) could be obtained for the crotonic compounds (C_1—C_2=C_3—R) by reacting with the three initiators. Crotonaldehyde is an exception. Radical spectrum A is assigned to the radicals produced by the addition of initiator radicals (R′) to carbon atom C_3. Esr spectrum B is assigned to radicals produced by the addition of initiator radicals R′ to carbon atom C_2. The concentration ratio of the two types of radicals depends on the substituents R of the crotonic compounds and the type of attacking radicals R′. As for the substituents of crotonic compounds, the ratio of A-type to B-type radicals decreases in the order CH_2OH > COOH > CN > CHO, which could be related to resonance effects of the substituents in the radicals formed which favors radical B. The ratio of A- to B-type radicals decreases generally in the order H_3C > HO > H_2N for R′, *i.e.*, decreases with increasing electron affinity of the attacking radicals R′.

The coupling constants of β protons vary considerably with the nature of the substituents. The β_1-coupling constants decrease in the order HO > H_3C > H_2N and CN > CHO > CH_2OH > COOH, *i.e.*, decrease with increased bulkiness of the groups.

The coupling constants of γ-CH_3 protons decrease in the order COOH > CHO > CH_2OH > CN and HO $\simeq$ H_3C > H_2N, which evidently is related to the spin density on the γ-CH_3 groups. The value of a_N in the series of R-$CH(CH_3)$-$\dot{C}H(CN)$ depends on the nature of R·. a_N varies with R in the order H_3C > HO > H_2N, *i.e.*, is decreased by electron-withdrawing substituents.

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