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ELECTRON-SPIN RESONANCE STUDIES OF OXIDATION, PHOTOSENSITIZED BY FERRIC CHLORIDE, OF SOME ALCOHOLS IN RIGID GLASSES

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ABSTRACT

Ferric chloride-photosensitized oxidations of methanol, ethanol, 1-propanol (**3**), 2-propanol, 1-butanol (**5**), 2-methyl-1-propanol, 2-methyl-2-propanol (**7**), 1-pentanol, cyclopentanol, and cyclohexanol were conducted in the cavity of an e s r spectrometer at temperatures between −150 and −196°, with a high-pressure, mercury lamp as the light source Except for rigid glasses of **7** plus ferric chloride, all of the photolyzed alcohols investigated generated e s r.-detectable free-radicals. The effects of temperature on the concentrations of the radicals formed in the rigid glasses indicated that the production of free radicals derived from alcohols involves an active intermediate trapped in the photolyzed, ferric chloride–alcohol rigid glass In almost all cases, the intensities of the signals of the e s r.-detectable radicals increased after photolysis was discontinued When the temperatures of the photolyzed, rigid glasses were increased, the intensities of the signals generated by the radicals increased initially, until radical recombinations became the predominant reaction Based on hyperfine splittings of the e s r spectra, a free-radical site could be assigned to the hydroxyl-bearing carbon atom of all of the alcohols investigated, except **3**, **5**, and **7**. As the temperatures of the rigid glasses were increased, changes in hyperfine splittings of the e s r spectra of the radicals derived from alcohols were observed, these changes probably reflect increased molecular motion of the photolyzed alcohols

INTRODUCTION

During an investigation of the effects of ultraviolet radiation on free-radical reactions initiated in cellulose[1], photosensitized oxidations of alcohols in aqueous solutions that contained sodium anthraquinonesulfonate sensitizers were studied at 25° by electron-spin resonance (e s r) spectroscopy The role and kinetics of semiquinone radicals and radical ions in photosensitized oxidation of alcohols were reported[2]

We have now applied these techniques to the elucidation of the nature of radicals derived from alcohols in rigid glasses during photosensitized oxidation at

-150 to $-196°$. For cellulose in the solid state, alcohols in rigid glasses are probably better models than alcohols in aqueous solution. Also, ferric chloride was used as the photosensitizer, it does not generate an e.s.r.-detectable intermediate. The nature of the photosensitizer-induced, free radicals in several alcohols in rigid glasses is described.

RESULTS AND DISCUSSION

Ferric chloride-photosensitized oxidations of methanol (**1**) and ethanol (**2**) in rigid glasses at $-175°$ gave free radicals that generated triplet and quintet e.s.r. spectra for $\cdot CH_2OH$ and $CH_3\dot{C}HOH$, respectively. The spectra also exhibited hyperfine sub-splittings of $\sim 400\ \mu T$ that were attributed to interactions of hydroxyl hydrogen atoms with the unpaired electrons. For both alcohols, the intensities of the e.s.r. spectra were stable at $-175°$. When the temperatures of the glasses were raised to $-160°$, the intensities of the spectra increased momentarily and then decreased to about 80% of their initial values. Sullivan and Koski[3] recorded a triplet e.s.r. spectrum for methanol photolyzed in a matrix at $-196°$; when they photolyzed ethanol in a matrix at $-196°$, an e.s.r. spectrum having very low intensity was recorded[4]. Gibson *et al.*[5] photolyzed a rigid glass of ethanol and hydrogen peroxide at $-196°$, and recorded an e.s.r. spectrum having very low stability and intensity.

When rigid glasses of ferric chloride plus water, methanol plus water, or ethanol plus water were photolyzed with light of wavelength 365.0 nm, no e.s.r.-detectable, radical intermediates were formed[6,7]. When rigid glasses of ferric chloride plus methanol or ethanol were photolyzed, e.s.r.-detectable radicals were formed. Our interpretation of the hyperfine splittings of the e.s.r. spectra is that the radicals derive

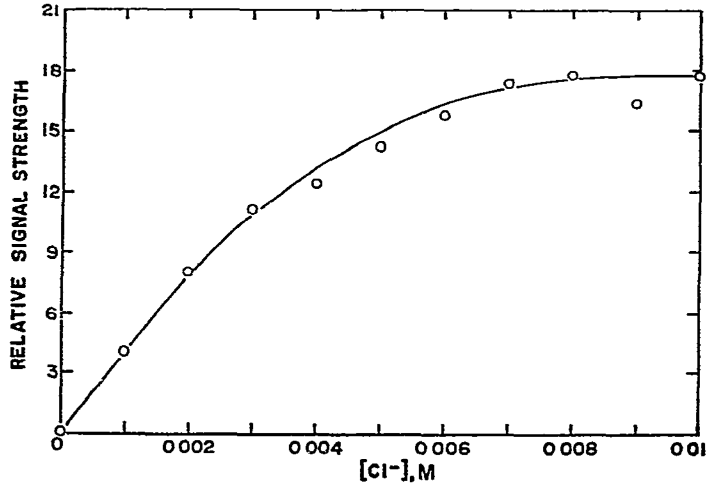

Fig. 1. Effect of [Cl$^-$] on the concentration of free radicals formed during ferric chloride-photosensitized oxidation of ethanol (**2**) for 4.5 min at $-170°$. (Composition of rigid glass, 99:1 (v/v) ethanol–water, 1mM $Fe(NO_3)_3$. LiCl added to obtain the desired [Cl$^-$].)

from the alcohols In ferric chloride-photosensitized reactions, mechanisms proposed for the derivation of active intermediates from ferric chloride involve the formation of $FeCl_4^-$ (ref 8) or Cl (refs. 6, 9, and 10). Subsequent reactions of these intermediates with alcohols by hydrogen-atom abstractions yield e s r -detectable free-radicals The effect of $[Cl^-]$ on the concentration of free radicals formed during ferric chloride-photosensitized oxidation of ethanol (2) in rigid glasses is shown in Fig 1 In rigid glasses of 99 1 (v/v) ethanol–water, $Fe(NO_3)_3$ (1mM), and LiCl, $[CH_3\dot{C}HOH]$ increased as [LiCl] increased The maximum $[CH_3\dot{C}HOH]$ was recorded at $[Cl^-]/[Fe^{3+}] \geqslant 7$. The change in color of the rigid glass indicated that Fe^{3+} was reduced to Fe^{2+} during photosensitized oxidation of the ethanol.

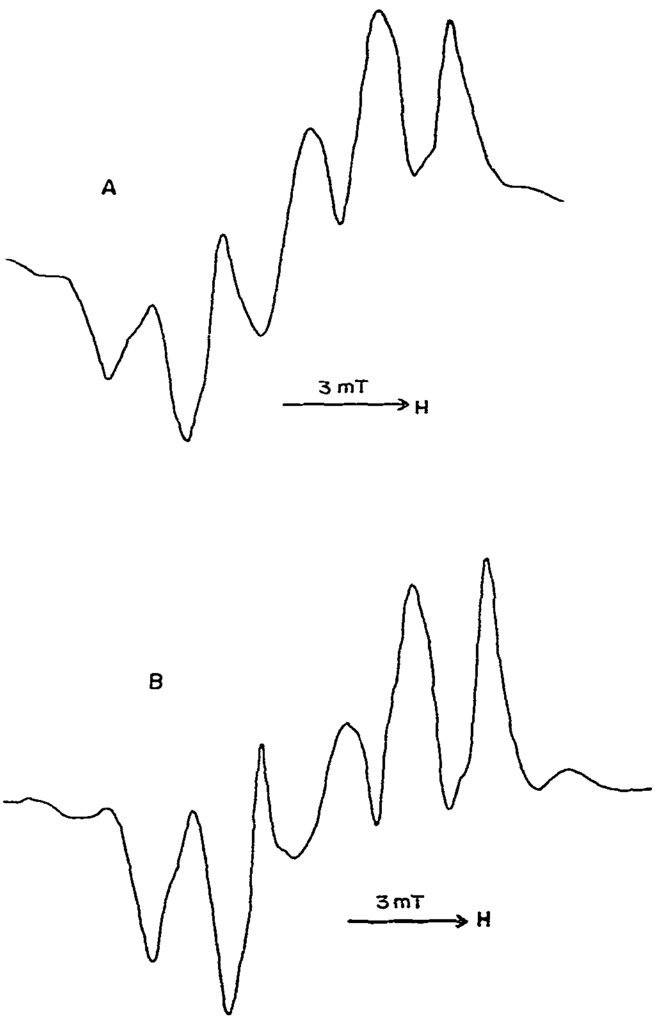

Fig 2

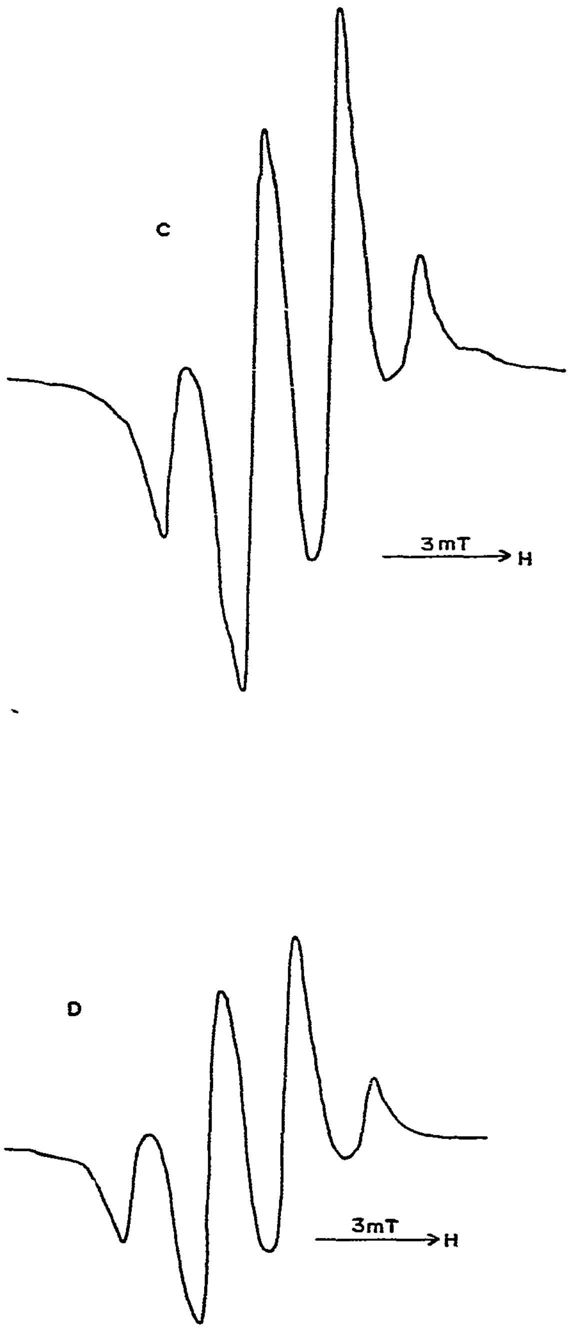

Fig 2 E s r spectra of photolyzed, rigid glasses of ferric chloride plus 1-propanol (3) (A, Photolyzed for 4 min at −175°, spectrum recorded at −175°, B photolyzed glass 2A warmed for 2 min to −160°, spectrum recorded at −175°, C, photolyzed glass 2B warmed for 3 min to −150°, spectrum recorded at −175°, and D, photolyzed glass 2C warmed for 3 min to −145°, spectrum recorded at −175°)

The stability of free radicals derived from 1-propanol (3) with increase in temperature was greater than that of free radicals derived from **1** or **2** The initial rate of free-radical formation in photolyzed 1-propanol glasses was much lower than in ethanol glasses at −175° The 1-propanol glasses had to be irradiated for 4 min at −175° to yield products that gave e s r -detectable signals The initial signal generated at −175° was a five-line spectrum (see Fig 2A) that did not have a binomial distribution of intensity Assuming that the α and β protons are almost equivalent, a radical of the type $\cdot CH_2CH_2CH_2OH$ could generate the spectrum observed Raising the temperature of the sample to −160° for 2 min and then relowering it to −175° resulted in a fivefold increase in signal intensity and a change in the number of lines from 5 to 7 (see Fig 2B) The seven-line spectrum was distorted, such a spectrum could be generated by $CH_3\dot{C}HCH_2OH$, having nearly equivalent α and β protons When the temperature of the sample was raised to −150° for 3 min and then relowered to −175°, the spectrum (Fig 2C) had 4 well-defined lines with 1 8-mT splittings When the temperature of the sample was raised to −145° for 3 min and then relowered to −175°, the spectrum shown in Fig 2D was recorded, its intensity had decreased ~45%, as compared with that of the spectrum shown in Fig 2C When the temperature of the sample was raised to −140° (data not shown), the intensity of the signal decreased sharply; the hyperfine splitting of the four-line spectrum did not change Evidently, the free radical $CH_3CH_2\dot{C}HOH$ generated the four-line e s r spectrum, and was the most stable of three types of radical derived from 1-propanol The α and β protons appeared to be nearly equivalent The distortions of the e s r spectra shown in Figs 2A and 2B are probably attributable to the co-existence of the three types of radical The major, hyperfine components of the spectra indicated that the least stable free-radicals preponderate at the lower temperatures The order of appearance of the three types of radical, as the temperature was increased, indicated that restricted accessibility of free-radical sites, caused by hydrogen bonding, might be important in the reaction of the intermediates from ferric chloride plus 1-propanol Accessibility of the more stable free-radical sites increased with temperature At the lowest temperature employed, the self-association of 1-propanol molecules by hydrogen bonding may restrict the accessibility of C-1

Before photolysis, rigid glasses of ferric chloride and 2-propanol (4) at −180° generated a broad, one-line, e s r spectrum After photolysis of the glass for 8 min at −180°, an e s r spectrum having seven lines was generated (data not shown). When the temperature of the rigid glass was raised to −150°, the intensity of the spectrum and the sharpness of the hyperfine splitting increased A radical of the type $CH_3\dot{C}OHCH_3$ would have six equivalent protons interacting with the unpaired electron on C-2, and should generate a symmetrical, seven-line spectrum, as shown in Fig 3 Evidently, the active intermediates formed during the photolysis of glasses of ferric chloride plus **4** selectively abstracted hydrogen atoms attached to C-2 The apparent energy of activation of the reaction of the active intermediates with 2-propanol to yield $CH_3\dot{C}OHCH_3$ was estimated from an Arrhenius plot to be about 21 kJ mole^{-1} This value approximates the energy of a hydrogen bond[11], and suggests that hydrogen-bond dissociation is the rate-determining step and occurs before the reaction of the active intermediates with 2-propanol to yield e s r.-detectable radicals

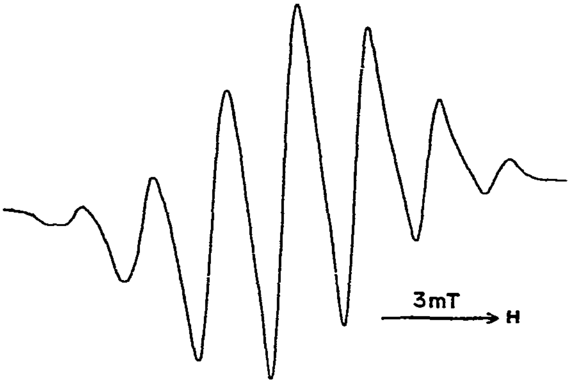

Fig 3 E s r spectrum of photolyzed, rigid glass of ferric chloride plus 2-propanol (4) (Photolyzed for 8 min at −180°; then the glass was warmed for 4 min to −150°, and the spectrum was recorded at −160°)

Photolyzed, rigid glasses of ferric chloride plus 1-butanol (5) generated a seven-line e s r. spectrum that exhibited hyperfine splittings similar to those of the spectrum derived from 2-propanol (4), see Fig 3 If the α and β protons of a radical of the type $CH_3\dot{C}HCH_2CH_2OH$ were nearly equivalent in coupling with the unpaired electron, a seven-line e s r. spectrum would be generated After photolysis for 8 min at −180°, the light was turned off, the concentration of e s r -detectable radicals continued to increase for as long as 90 min This indicated that the active intermediates formed during the photolysis continued to react with 1-butanol in the absence of light There was no e s r. evidence for radicals located at C-1, C-2, or C-4 of 1-butanol

Photolyzed, rigid glasses of ferric chloride plus 2-methyl-1-propanol (6) initially generated a three-line e s r spectrum having hyperfine splittings of ~1 7 mT (data not shown). After photolysis for 8 min at −180°, the light was turned off, the concentration of e s r -detectable radicals increased as the temperature of the glass was then increased, and the e s r spectrum changed from a three- to a multi-line spectrum that indicated that unpaired electrons were located at more than one carbon site For example, a radical of the type $CH_3(CH_3)CH\dot{C}HOH$ could generate a three-line e s r spectrum, if the α and β protons were nearly equivalent A radical of the type $CH_3(CH_3)\dot{C}CH_2OH$ could generate a multi-line e s r spectrum

Photolyzed, rigid glasses of ferric chloride and 2-methyl-2-propanol (7) did not generate an e s r.-detectable radical. After photolysis, the glasses were colorless, and this indicated that Fe^{3+} was reduced to Fe^{2+}. When glasses that contained about 10% (v/v) of water were photolyzed, a three-line e s r. spectrum was generated (data not shown). A radical of the type $(CH_3)(CH_3)(\dot{C}H_2)COH$ formed by abstraction of hydrogen from one of the CH_3 groups would generate a three-line e s r spectrum. Addition of water to the glass may have increased hydrogen bonding in the system, thereby tending to stabilize the primary radical Harris *et al* [12] reported that the length of hydrogen-bond chains in liquid 2-methyl-2-propanol is limited to <5 molecules. The addition of water would tend to increase hydrogen bonding in 2-methyl-2-propanol

Photolyzed, rigid glasses of ferric chloride plus pentanol (**8**) generated a nine-line e s r spectrum having an overall, hyperfine splitting of 16 2 mT (data not shown). Photolyzed, rigid glasses of ferric chloride plus cyclopentanol (**9**) also generated a nine-line e s r spectrum, having an overall, hyperfine splitting of 17 5 mT Assignments of structures to radicals were not possible The ring structure of cyclopentanol and, possibly, the conformation of the long chains of hydrogen-bonded pentanol could cause protons to exhibit restricted rotation about C–C bonds Wide variations in hyperfine coupling of *β* protons are reported to occur when protons experience restricted rotation[7,13] The effects of nonequivalent *β* protons on hyperfine splitting, and the possibility of the formation of more than one type of free radical, probably account for the generation of the complex, e s r spectrum

Photolyzed, rigid glasses of ferric chloride plus cyclohexanol (**10**) generated a nine-line e s r spectrum having an overall, hyperfine splitting of about 11 mT When the temperatures of the photolyzed glasses were increased slightly, reaction of the active intermediates with cyclohexanol generated the nine-line e s r spectrum shown in Fig 4 Lines 2, 5, and 8 constitute a three-line spectrum having hyperfine splittings of about 3 6 mT Lines 1 and 3, 4 and 6, and 7 and 9 form two-line spectra having hyperfine splittings of about 1 8 mT These three sets of lines also form a triplet

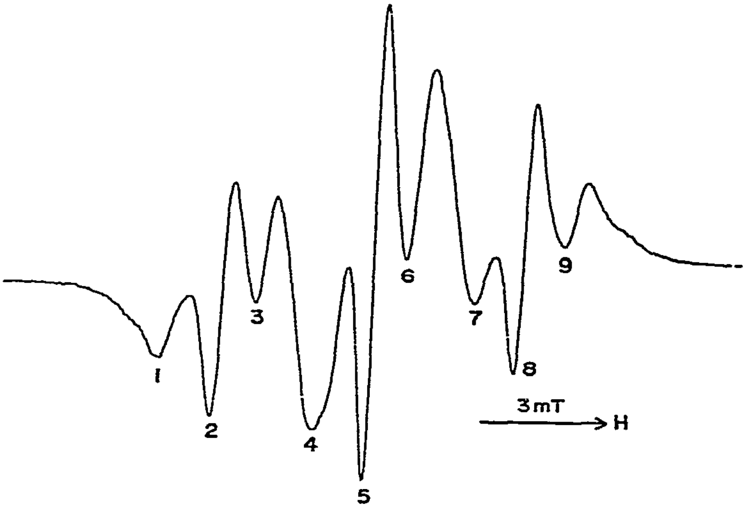

Fig 4 E s r spectrum of photolyzed, rigid glass of ferric chloride plus cyclohexanol (**10**) (Photolyzed for 10 min at −196°, then the glass was warmed for 50 sec at 25°, and the spectrum was recorded at −196°)

spectrum having hyperfine splittings of ~3 6 mT. The most stable conformation for cyclohexanol should be that chair conformation having the hydroxyl group equatorially attached[14]. The magnitude of the β-proton coupling varies with the orientation of the β CH bond relative to the nodal plane of the unpaired electron, and is close to zero when the β CH bond lies in the nodal plane[12]. The coupling from equatorial protons in cyclohexanol should be close to zero Therefore, the three-line spectrum (lines 2, 5, and 8) is probably generated by a free radical on C-1 that interacts with the axial protons on C-2 and C-6 Two-line spectra (lines 1 and 3, 4 and 6, or 7 and 9) would be generated by a free radical located on any carbon atom other than C-1 A two-line spectrum having a hyperfine splitting of 1 8 mT would result from the interaction of the α proton with the unpaired electron. The interaction of the β protons (equatorially attached to adjacent carbon atoms) with the unpaired electron would generate the three sets of lines (lines 1 and 3, 4 and 6, and 7 and 9) that form a triplet spectrum having hyperfine splittings of ~3 6 mT. The e s r spectrum shown in Fig 4 is, then, the summation of spectra generated by a free radical situated on C-1 and a free radical on one of the other carbon atoms

Photolyzed, rigid glasses of ferric chloride with each of the alcohols investigated, except 2-methyl-2-propanol, evidently contained trapped, active intermediates When made with water, however, glasses of 2-methyl-2-propanol with ferric chloride generated trapped, active intermediates on photolysis In the photolyzed, rigid glasses of ferric chloride with the alcohols investigated, hydrogen bonding was evidently a factor in stabilizing the trapped, active intermediates derived from ferric chloride Rigid glasses of ferric chloride with an alcohol should constitute a satisfactory model for cellulose in the solid state Natural cellulose in the solid state is a hydrogen-bonded network[15] of a polymeric alcohol

EXPERIMENTAL

The alcohols and the ferric chloride, ferric nitrate, and lithium chloride used were of reagent grade The rigid glasses were frozen solutions (4mM) of ferric chloride in neat alcohols, except in the two cases indicated Distilled water was used in the preparation of one rigid glass

The e s r spectra were recorded with a Varian 4502-15 EPR spectrometer* equipped with a variable-temperature accessory permitting operation from −185 to +300° A Dewar accessory for liquid nitrogen permitted operation at −196° Spectra were recorded at the temperatures indicated, in the form of the first derivative of the absorption line

Solutions of ferric chloride in an alcohol that had been purged free of oxygen were placed in quartz tubes, quickly frozen in liquid nitrogen, and then placed directly in the resonant cavity of the spectrometer, the temperatures of the rigid

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Trade names are given as part of the exact experimental conditions, and not as an endorsement of the products over those of other manufacturers glasses were controlled as indicated The rigid glasses were photolyzed by exposure to light that passed through a slotted opening in the resonant cavity A PEK 110, mercury short-arc, point-source, high-pressure lamp that was operated at 100 W was used to irradiate the rigid glasses The light was focused to about 1 cm^2 on the slotted opening in the resonant cavity, and had a rated luminous intensity of $\sim$140 kcd cm^{-2} The activated intermediates formed from ferric chloride reacted with the alcohols to generate e s r -detectable radicals After photolysis, increases in temperatures of the photolyzed glasses increased the extent of reaction of the active intermediates with the alcohols to yield higher concentrations of e s r -detectable radicals, as reported previously for alcohols and vinyl monomers[3,6,7,16].

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