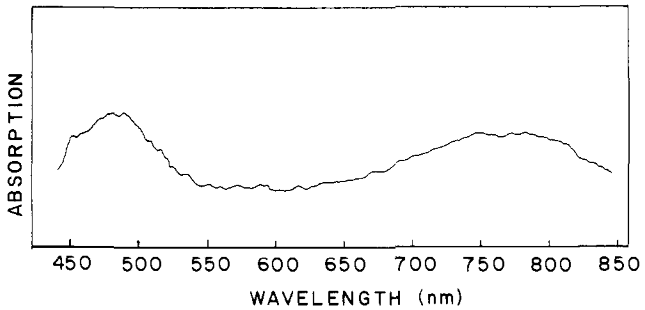

Figure 1. Transient absorption spectra following photolysis of [Mn$_2$(CO)$_{10}$] in ethanol. The transient absorption spectra are probed 25 ps after photolysis. The absorbance at 480 nm is 0.15.

band cannot therefore be the result of [Mn$_2$(CO)$_{10}$] homolysis; since it is formed in 25 ps, and is therefore unlikely to be a secondary product, we conclude that it must be assigned to a second primary photoproduct. One possible assignment is to a dimanganese species such as [Mn$_2$(CO)$_9$(EtOH)], which could be formed by loss of CO and coordination of a solvent molecule.[7] The absorption spectrum of the related molecule [Mn$_2$(CO)$_9$(pyr)] (pyr = pyridine) has recently been reported to contain a band at 450 nm,[8] and the difference in $\lambda_{\max}$ values is not unreasonable given the range of values reported for the $d\pi \rightarrow \sigma^*$ transition for other [Mn$_2$(CO$_9$)L] complexes.[9,10] It is, however, entirely possible that the band observed in the present experiment is due to a carbonyl bridged species such as that proposed by Pöe.[11]

The solution photolyses of both [Mn$_2$(CO)$_{10}$] and [Re$_2$(CO)$_{10}$] have been studied previously by a number of groups, and they are generally taken as prototypical of the photoreactions of organometallic compounds containing metal-metal bonds.[2-4,11-14] It has been reported that irradiation of the metal-metal $\sigma \rightarrow \sigma^*$ transition results in homolysis of the metal-metal bond,[13] but kinetic analysis of the photolysis of [Mn$_2$(CO)$_{10}$] in the presence of CCl$_4$ has led to the suggestion that there are in fact two primary photoprocesses.[11] One of these is the homolysis reaction, while the second was proposed to be isomerization of [Mn$_2$(CO)$_{10}$] to a form containing one or more bridging carbonyl ligands. The most recent flash photolysis studies,[3] however, have not supported these conclusions and were interpreted in the terms of exclusive homolysis. We were unable to reproduce earlier observations[4] of a second long-lived intermediate in addition to [Mn(CO)$_5$]·. Our results indicate that there are in fact two primary photoproducts as suggested by Pöe,[11] but it is unclear whether we are observing the same species reported by Hughey et al.[4] since that species was only observed after repeated irradiation. Our suggestion that the second species is formed by CO loss is consistent with recent results on photolysis of other metal-metal bonded species containing carbonyl ligands, which indicated that two primary photoprocesses were occurring and were interpreted in terms of competitive cleavage and CO loss.[15,16]

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Registry No. Mn$_2$(CO)$_{10}$, 10170-69-1.

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Chemical Effects of Ultrasound on Aqueous Solutions. Evidence for ·OH and ·H by Spin Trapping

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Ultrasound is widely used in diagnosis[1] and therapy[2] in medicine, and the chemical effects of ultrasound on aqueous solutions have long been of interest.[3] Intense ultrasound has been reported to cause chemical damage through the phenomenon of cavitation.[4-9] Cavitation produces high local instantaneous temperatures and pressures and sonoluminescence.[3,5] In sonolysis studies of aqueous solutions, it has been proposed that hydroxyl radicals (·OH) and hydrogen atoms (·H) are produced by ultrasound.[10-19] In the present spin-trapping and ESR study, we report conclusive evidence for the formation of ·OH and ·H during sonolysis of aqueous solutions. Hydroxyl radicals are known to be responsible for the reproductive death of mammalian cells exposed to ionizing radiation.[20,21]

In spin trapping[22-24] a diamagnetic nitroso or nitrone compound (the spin trap) is used to convert short-lived radicals into relatively longer lived nitroxyl radicals that are ESR observable. Recently, it has been demonstrated[25] that free radicals produced by sonolysis of carbon tetrachloride, but not of aqueous solutions, can be spin trapped by 2-methyl-2-nitrosopropane and identified by ESR. In the present work, nonvolatile nitrone spin traps[26]

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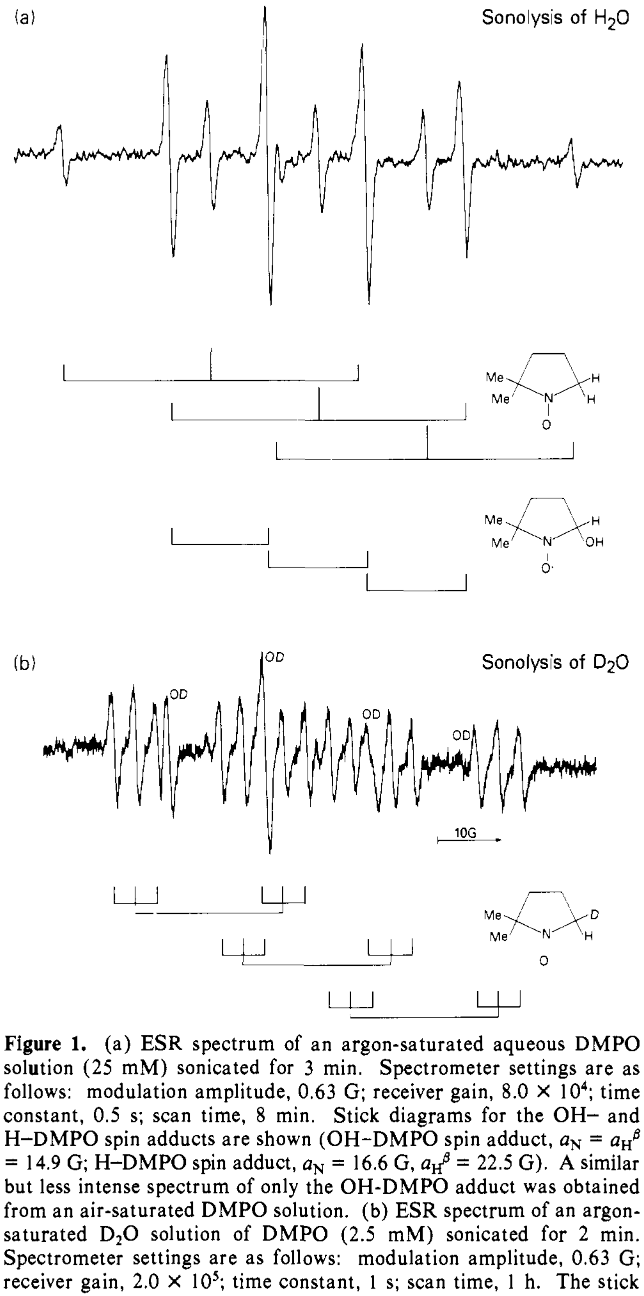

Figure 1. (a) ESR spectrum of an argon-saturated aqueous DMPO solution (25 mM) sonicated for 3 min. Spectrometer settings are as follows: modulation amplitude, 0.63 G; receiver gain, 8.0 × 10^4; time constant, 0.5 s; scan time, 8 min. Stick diagrams for the OH– and H–DMPO spin adducts are shown (OH–DMPO spin adduct, $a_N = a_H{}^\beta$ = 14.9 G; H–DMPO spin adduct, a_N = 16.6 G, $a_H{}^\beta$ = 22.5 G). A similar but less intense spectrum of only the OH-DMPO adduct was obtained from an air-saturated DMPO solution. (b) ESR spectrum of an argon-saturated D_2O solution of DMPO (2.5 mM) sonicated for 2 min. Spectrometer settings are as follows: modulation amplitude, 0.63 G; receiver gain, 2.0 × 10^5; time constant, 1 s; scan time, 1 h. The stick diagram for the D–DMPO spin adduct is shown (D–DMPO spin adduct, a_N = 16.6 G, $a_H{}^\beta$ = 22.5 G, $a_D{}^\beta$ = 3.4 G). The OD–DMPO spin adduct (lines labeled OD) decayed during the 1 h scan.

(DMPO,[27-30] PYBN,[31] and POBN[29,32]) were used. DMPO was purified as described previously,[33] and its concentration was measured by UV spectroscopy.[34] Samples (3 mL) were sonicated in a Bransonic 12 ultrasonic bath[25] (frequency, 50 kHz; intensity, 6 × 10^2 W/m^2 for air-saturated water) at room temperature with argon gas bubbling (flow rate, 0.5 L/min) to enhance the radical yield.[19] ESR spectra were recorded on a Varian E-9 X-band spectrometer. In Figure 1a, the ESR spectrum obtained from a sonicated aqueous DMPO solution is displayed. The spectrum consists of OH and H adducts as indicated by the stick diagrams, implying that ·OH and ·H are created by the sonolysis of water. Similar experiments with PYBN led to the same conclusion. OH and H adducts of DMPO or PYBN are known to be stable.[27-30] Only hydrogen atoms could be observed with POBN since the lifetime of the OH–POBN adduct is of the order of seconds.[29] In the ESR spectra obtained from the sonolysis of D_2O solutions containing either DMPO, PYBN, or POBN, a secondary triplet with equal intensity due to the spin-trapped D atom was observed, hence confirming the formation of H atoms from water. In Figure 1b, the ESR spectrum of spin adducts generated from a sonicated D_2O solution of DMPO is shown. Experiments on the effects of increasing the spin-trap concentration on the ESR signal intensity of the OH-DMPO and H-POBN adducts showed increasing yields, which reached a plateau and remained constant above about 1 mM DMPO and 10 mM POBN. This behavior is consistent with the formation of the adducts by a free-radical mechanism. When aqueous solutions containing either DMPO (3.2 mM) or POBN (20 mM) were sonicated, the ESR intensities increased linearly with time and then reached a plateau at 15 and 30 min, respectively. The amounts of the spin adducts were determined by using a stable nitroxide radical, 3-carbamoyl-2,2,5,5-tetramethylpyrrolidin-1-yloxy. The resulting values are 0.18 μM at 3 min and 0.67 μM in the plateau region for OH–DMPO adduct and 0.05 μM at 3 min and 0.22 μM in the plateau region for H–POBN adduct. In the present study, all samples were sonicated for 3 min, which falls in the linear region of the plot of the ESR intensities of the spin adduct signals vs. sonication time.

Three reactions have been reported to produce hydroxyl and hydrogen adducts of DMPO, PYBN, and POBN by reaction pathways not involving the formation of ·OH and ·H. First, DMPO is converted into the isomeric oxazirane by photochemical rearrangement which subsequently leads to the OH–DMPO adduct by hydrolysis and oxidation.[36] Second, the hydroxyl adduct of POBN could be formed by acid-catalyzed addition of water followed by H_2O_2 oxidation.[31] Third, the hydrogen adducts could be produced by the reaction of e_{aq}^- with all three spin traps followed by protonation.

In order to verify that ·OH and ·H are generated from water by ultrasound, experiments in which scavengers compete with the spin traps for these radicals were carried out. The rate constants of the reactions of $HCOO^-$ and C_2H_5OH with ·OH, ·H, and e_{aq}^- are well established.[37-39] In Figure 2, the spectral changes of sonicated aqueous DMPO solutions containing various concentrations of sodium formate are displayed. As the sodium formate concentration is increased at constant DMPO concentration, a decrease in the signal of the OH–DMPO adduct and a corresponding increase of the CO_2^-–DMPO adduct[40] was observed, indicating competitive scavenging of ·OH by DMPO and HCO-

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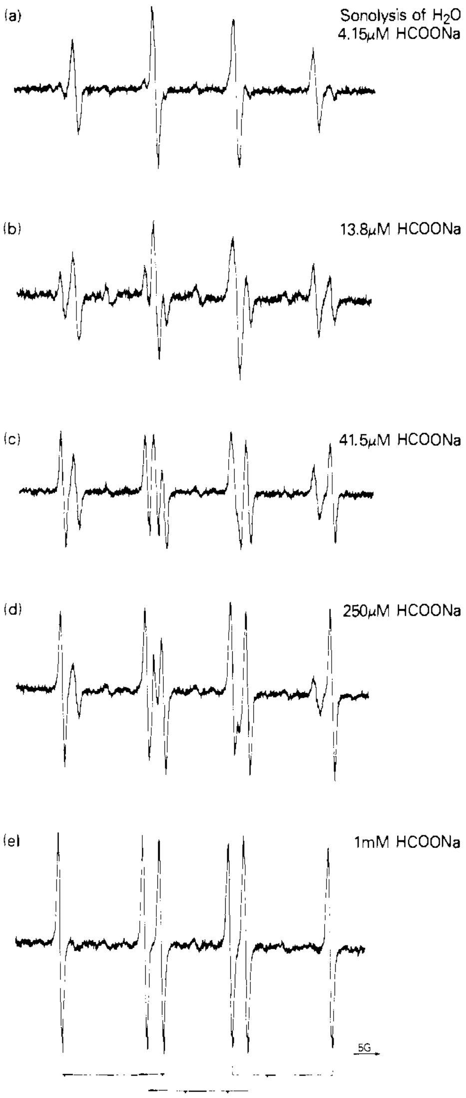

Figure 2. ESR spectra of sonicated (3 min) argon-saturated aqueous solutions containing DMPO (250 μM) and various sodium formate concentrations. At this DMPO concentration the H-DMPO spin adduct signal is negligible. A stick diagram for the CO_2^-–DMPO spin adduct is shown.

O^-.[41,42] Similarly, when aqueous POBN solutions containing sodium formate were sonicated, a decrease of the H–POBN adduct and an increase of the CO_2^-–POBN adduct were observed with increase in formate concentration. Analogous evidence was obtained with the formation of $CH_3CH(OH)$ adducts[28] when ethanol was used as a scavenger in the presence of DMPO or POBN. Since ethanol does not react with e_{aq}^-,[39] this result suggests that the H adducts are formed from ·H. Further support for this result was obtained when aqueous POBN solutions (25 mM) containing $CdSO_4$ (300 μM), a well-known e_{aq}^- scavenger,[39] were sonicated. The signal intensity of H–POBN adduct was not decreased, indicating no formation of e_{aq}^-. The effects of various volatile and nonvolatile radical scavengers and of dissolved gases on the radical yields will be the subject of forthcoming publications.

Registry No. H·, 12385-13-6; HO·, 3352-57-6; OH-DMPO spin adduct, 55482-03-6; H-DMPO spin adduct, 40936-29-6; OH-PYBN spin adduct, 69397-28-0; H-PYBN spin adduct, 69397-35-9; H-POBN spin adduct, 81616-73-1.

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[42] The observed changes in the ESR spectra occur when the product, $k_{HCOO^-+\cdot OH}[HCOO^-]$, is comparable to $k_{DMPO+\cdot OH}[DMPO]$.

Reductive Cleavage of Glycosides

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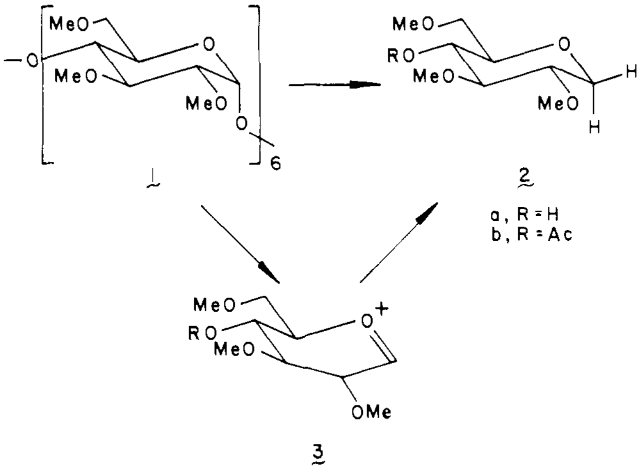
The technique of "methylation analysis" is routinely employed in the structural characterization of complex carbohydrates as a means to establish the linkage positions of the constituent monosaccharides. This method is based on the ability to fractionate and characterize the partially methylated monosaccharides generated via hydrolysis of the fully methylated polysaccharide, which is accomplished most conveniently by combined gas–liquid chromatography/mass spectrometry of their alditol acetate derivatives.[1] This method suffers the disadvantage, however, that hydrolysis of the fully methylated polysaccharide permits furanose–pyranose equilibration in many of the resultant partially methylated monosaccharides and therefore the loss of the desired structural information. On the basis of methylation analysis, for example, one cannot distinguish between a 4-linked *aldohexopyranose* residue and a 5-linked *aldohexofuranose* residue, as both give the same partially methylated sugar (2,3,6-tri-*O*-methylhexose) after hydrolysis of the glycosidic linkage. The same problem is encountered with 4- and 5-linked aldopentose residues and 5- and 6-linked ketohexose residues.

Although methods are available for distinguishing between furanose and pyranose residues in polysaccharides,[2-4] their application is laborious and in some cases inconclusive, especially in cases where both ring forms are present in substantial proportions. We therefore sought to develop a method, based on methylation analysis, that would allow us to simultaneously determine the position of linkage *and* the ring form of each monosaccharide residue in a polysaccharide. A route involving cleavage of the glycosidic carbon–oxygen bond by a hydride equivalent, as in the conversion of **1** to **2a** would be particularly advantageous because (1) the ring form of the monosaccharide residue would be preserved, (2) a stable anhydroalditol would be generated, and (3) for aldoses at least, a mixture of anomers would not be formed. Ionic hydrogenation with triethylsilane in trifluoroacetic acid, which has been shown to effect the reduction of other acetals and ketals,[5] seemed to potentially be an attractive means of accomplishing this type of conversion. Treatment of



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