

Paramagnetic Resonance Study of Liquids during Photolysis.

III. Aqueous Solutions of Alcohols with Hydrogen Peroxide¹

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Abstract: Paramagnetic resonance spectra of free radicals have been studied in aqueous solutions of alcohols containing hydrogen peroxide during the course of irradiation with ultraviolet light. The addition of water to *t*-butyl, isopropyl, and ethyl alcohols enhanced the formation of the radicals resulting from abstraction of β hydrogens. The principal effect of acidifying the solutions was the enhancement of the rate of exchange of hydroxyl protons. Hyperfine couplings and *g* values were measured for $(\text{CH}_3)_2(\dot{\text{C}}\text{H}_2)\text{COH}$ and $\text{CH}_3(\dot{\text{C}}\text{H}_2)\text{CHOH}$. The primary product from allyl alcohol was the radical resulting from α -hydrogen abstraction whether or not water and acid were added. The primary product from ethylene glycol with or without water was $\dot{\text{C}}\text{HOHCH}_2\text{OH}$, but with small amounts of acid this radical was not obtained. In its place was $\dot{\text{C}}\text{H}_2\text{CHO}$. Hyperfine couplings and the *g* value were measured and discussed in terms of an aldehyde structure which is preferred and the isomeric ring structure.

We recently studied² paramagnetic resonance spectra of simple radicals formed by abstraction of hydrogen from various alcohols. Alcohol solutions containing a small amount of H_2O_2 were photolyzed with ultraviolet light causing the OH radical to be formed from H_2O_2 which in turn abstracted hydrogen from the alcohol. The radicals were observed at steady-state concentration during continuous photolysis of the solution as it flowed through the microwave cavity of the spectrometer. Oxygen had to be excluded in most cases in order to prevent the formation of peroxy radicals. A number of the radicals had previously been studied by Dixon and Norman³ using a rapid flow and mixing technique. This method also involved hydrogen abstraction by the OH radical, but it differed from the photolytic method in the way OH was generated. The OH was formed by mixing an aqueous solution containing titanous ion (and H_2SO_4) with a dilute aqueous solution of H_2O_2 . The alcohol of interest was added to each of these aqueous solutions. Once the solutions were mixed, they had to be flowed very rapidly into the active region of the microwave cavity. We commented on a number of differences in the results obtained by the two methods. These differences have now been examined in somewhat more detail, and the results are reported in this paper.

A number of the radicals made by photolysis² gave well-resolved hyperfine splittings for the hydroxyl hydrogen in contrast to spectra for the same radicals prepared by rapid mixing.³ This difference was attributed to the more rapid exchange of the hydroxyl hydrogen in the acid media normally employed in the rapid mixing method. Recently we have studied⁴ this exchange in some detail for the radicals $\dot{\text{C}}\text{H}_2\text{OH}$ and $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$. Fischer⁵ has observed the hydroxyl proton splitting in $\dot{\text{C}}\text{H}_2\text{OH}$ using the rapid-mixing method and has also studied the dependence on pH. Apart from this difference in the hydroxyl proton splittings, there were basic differences in the chemistry of the systems studied.

The OH radical seemed much more specifically to abstract the hydrogen in the position α to the hydroxyl group in the photolytic experiments. We have now altered the conditions of the photolytic experiments, primarily by changing the amount of water present and the acid concentration, to see if the nature and distribution of radicals would be more nearly like that obtained by the rapid-mixing method.

Experimental Section

The microwave spectrometer operated at a nominal frequency of 9.5 GHz using 100-kHz field modulation. The experimental arrangement was exactly as described earlier² except that the original spectrometer using a magic tee was converted to one using a circulator,⁶ and the quality of the lenses used with the light source was improved. These changes gave a moderate improvement in sensitivity over that previously available. The same methods were used for making measurements and calculating hyperfine splittings and *g* values giving estimated error limits of ± 0.03 gauss and ± 0.00004 , respectively, unless otherwise indicated.

The sample handling system has also been described.² Each solution was freed of dissolved oxygen by purging with gaseous helium. It then flowed through a heat exchanger and thence through a silica cell located in the microwave cavity and was photolyzed as it passed the active region of the cavity. The temperature was measured as the liquid left the cavity. Also consistent with our earlier work,^{2,4} we label carbon positions as α , β , or γ depending upon their location with respect to the OH group.

All solutions contained 1% H_2O_2 by volume and were purged with helium unless otherwise indicated. Reagents were used as purchased, and their sources were the same as indicated in earlier work.^{2,4}

Results and Discussion

***t*-Butyl Alcohol.** We have been unable to find radicals during photolysis² of pure *t*-butyl alcohol containing small amounts of H_2O_2 . The alcohol has been useful as an inert solvent because of this stability toward loss of β hydrogens. In the presence of water, however, there is a small yield of $(\text{CH}_3)_2(\dot{\text{C}}\text{H}_2)\text{COH}$. A solution of 75% *t*-butyl alcohol and 25% H_2O (and H_2O_2) gave a very small yield of the above radical. A 50% solution gave a slightly stronger spectrum, but in both cases the spectra were too weak to measure satisfactorily. The addition of acid greatly improved the signal intensity. The effect could largely be a consequence of rapid exchange⁴ of hydroxyl hydrogens which

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966).

(3) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

(4) H. Zeldes and R. Livingston, *J. Chem. Phys.*, **45**, 1946 (1966).

(5) H. Fischer, *Mol. Phys.*, **9**, 149 (1965).

(6) E. A. Faulkner, *J. Sci. Instr.*, **39**, 135 (1962).

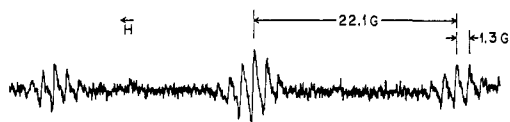


Figure 1. The spectrum of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ at 31° formed by photolysis of a solution containing equal volumes of *t*-butyl alcohol and water, 1% H_2O_2 , and 27 ml of concentrated H_2SO_4 /l. of solution.

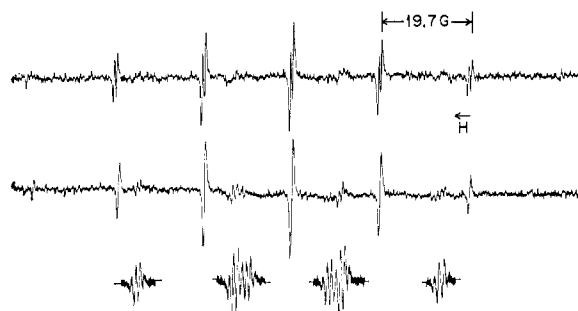


Figure 2. Spectra obtained by photolysis of a solution of 75% isopropyl alcohol and 25% water to which was added 1% H_2O_2 : top, spectra at about 30° showing strong doublets from $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ and very weak lines from $\text{CH}_3\dot{\text{C}}\text{HOH}$; middle, spectra at about 30° with 30 ml of concentrated H_2SO_4 added/l. of solution (the strong lines are from $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ where the hydroxyl proton hyperfine interaction has been averaged by rapid exchange. The lines from $\text{CH}_3\dot{\text{C}}\text{HOH}$ are more prominent than in the top spectrum); bottom, lines from $\text{CH}_3\dot{\text{C}}\text{HOH}$ at -5° with the same composition used for the middle spectra. Each group of lines is slightly expanded and centered under its approximate location in the spectra above.

is catalyzed by acid. In the limit of very fast exchange the hyperfine splitting from the hydroxyl hydrogen vanishes, components superimpose, and the lines become sharp. The spectrum obtained from such a solution containing 27 ml of concentrated H_2SO_4 /l. of solution is shown in Figure 1. Only five of the expected seven components in each bundle of lines are sufficiently strong to see. The parameters measured for $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ in this solution at 31° and with slightly reduced accuracy because of the low signal strength were $a(\text{CH}_3) = 1.33$ and $a(\text{CH}_2) = 22.06$ gauss, and $g = 2.00241$. Dixon and Norman³ obtained a stronger spectrum using the rapid-mixing technique and reported couplings of 1.3 and 21.3 gauss.

Isopropyl Alcohol. A strong spectrum of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ was obtained from the photolysis of pure isopropyl alcohol containing a small amount of H_2O_2 , but none of the radical formed by β -hydrogen abstraction was observed.² Upon photolyzing a solution containing 25% H_2O , the stronger lines of $\text{CH}_3\dot{\text{C}}\text{HOH}$ could just be made out as shown in the top spectrum of Figure 2. Five of the seven doublets of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ show prominently in this spectrum. The doublet splitting is due to the hydroxyl hydrogen interaction. With a solution containing 50% H_2O , the $\text{CH}_3\dot{\text{C}}\text{HOH}$ could be more easily made out. Upon adding acid, the spectrum from this radical became more prominent as shown in the middle of Figure 2. As with *t*-butyl alcohol this improvement could come largely from the averaging of the hydroxyl proton hyperfine interaction through rapid exchange. Note that this effect has caused the prominent doublets of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$

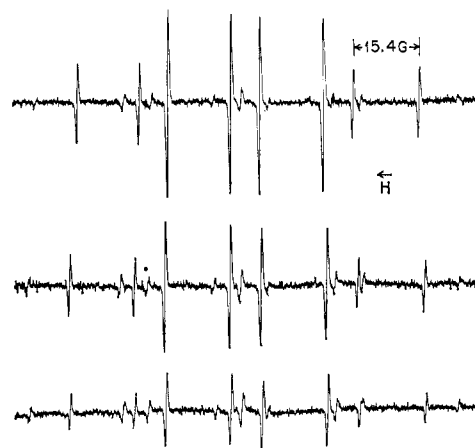


Figure 3. Spectra obtained by photolysis of solutions of ethyl alcohol and water containing 1% H_2O_2 and at about 30° . The water content from top to bottom was 25, 50, and 75%. The eight strong lines are from $\text{CH}_3\dot{\text{C}}\text{HOH}$ and the remaining lines are from $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$. The same spectrometer settings were used for all spectra.

to become single lines. Upon cooling the solution, line intensities became much greater as illustrated in the bottom of Figure 2. Each bundle of lines is slightly expanded but roughly centered under its correct location in the spectra that appear above.

The spectrum of $\text{CH}_3\dot{\text{C}}\text{HOH}$ was measured at -5° in a solution of 75% isopropyl alcohol and 25% H_2O to which 1% H_2O_2 and 30 ml/l. of concentrated H_2SO_4 had been added. The parameters found were: $a(\text{H}) = 24.38$, $a(\text{CH}_2) = 22.06$, and $a(\text{CH}_3) = 0.73$ gauss, and $g = 2.00236$. The spectrum for this radical observed by the rapid-mixing method³ was a weak quartet; the individual components shown in the bottom of Figure 2 were not resolved. A value of 22.0 gauss was reported for $a(\text{H})$ and $a(\text{CH}_2)$.

Ethyl Alcohol. Photolysis of ethyl alcohol³ containing a small amount of H_2O_2 gave a strong spectrum of $\text{CH}_3\dot{\text{C}}\text{HOH}$ which consisted of eight lines with relative intensities 1:1:3:3:3:3:1:1. The splitting from the hydroxyl hydrogen was not resolved at room temperature nor was the spectrum of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$ observed. At low temperatures, where radical lifetimes became longer and signals more intense, the spectrum of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$ was observed and measured. We have now found that the presence of water greatly enhances the relative yield of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$. This is illustrated in Figure 3. The strong lines of the top spectrum (75% ethyl alcohol) arise from $\text{CH}_3\dot{\text{C}}\text{HOH}$. This spectrum, as is normally the case, becomes weaker as the alcohol becomes more dilute. The weak lines of the top spectrum arise from $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$, and it is evident that not only on a relative but on an absolute basis they become stronger in the more dilute solutions illustrated in Figure 3. The relative intensities of the nine lines for this radical should be 1:2:2:1:4:1:2:2:1. The addition of acid (7 and also 21 ml of concentrated H_2SO_4 per liter of solution) to the 75% ethyl alcohol solution gave a small enhancement of the signal strength for $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$, but the effect was not striking. Parameters have been reported for $\text{CH}_3\dot{\text{C}}\text{HOH}$ in ethyl alcohol at several temperatures² and in various solvents⁴ at room temperature. There were variations in the values of the hyperfine couplings. It is evident

from Figure 3 that parameters for one or both of the radicals must be changing with water content. This can be seen easily by noting the second from the lowest field line of $\dot{\text{C}}\text{H}_2\dot{\text{C}}\text{HOH}$ and a nearby line from $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$ which are completely resolved in the top spectrum and merged in the bottom spectrum. A strong spectrum for $\text{CH}_3\dot{\text{C}}\text{HOH}$ was obtained by Dixon and Norman³ using rapid mixing. The spectrum of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$ was not reported, although a central line that appears in their published spectrum may come from this radical.

Allyl Alcohol. The two geometric isomers of the radical formed by abstracting the α hydrogen from allyl alcohol have been observed and measured.² This radical was not formed in significant yield by the rapid-mixing technique.³ Instead, the OH added to the double bond. We have added water and acid to allyl alcohol, but have not been able to greatly alter the products formed. A series of compositions was tried always maintaining the H_2O_2 at 1%. With 25% H_2O , the spectrum remained unchanged except for a small decrease in intensity. Adding 1 and also 6 ml of H_2SO_4 /l. of solution gave weaker but somewhat broader lines due to exchange of hydroxyl protons. With 50% water and still stronger acid the lines broadened to the point where the hydroxyl hyperfine splitting was no longer resolved. A few extraneous lines that were broad, complex, and weak were present, but it was not clear whether or not these represented a small yield of the radicals formed by addition of OH to the double bond. In any case, we could not obtain a spectrum resembling that obtained by the rapid-mixing technique.³

Ethylene Glycol. Photolysis of ethylene glycol² containing a small amount of H_2O_2 gave a spectrum of 24 sharp lines arising from $\dot{\text{C}}\text{HOHCH}_2\text{OH}$. Water was also added up to the point where the system was about 75% H_2O , and it was reported that this gave only a progressive weakening of the spectrum. We have now found that there are extra lines in the presence of water that come from at least two additional radicals. These spectra escaped detection in earlier work. They were too weak and poorly defined to warrant detailed study. Upon adding acid, even in small amounts, the spectra changed dramatically. For example, adding 0.5 ml of concentrated HCl /l. of a 50:50 water and ethylene glycol solution was adequate to bring about the change. The prominent spectrum of $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ vanished completely, and in its place were three prominent broad lines in the approximate intensity ratio of 1:2:1. It appeared that some of the very weak lines present before adding acid grew in intensity to give this triplet. In addition to these prominent lines there were very weak lines from another radical.

These results are consistent with Dixon and Norman's³ observations using the rapid-mixing technique. They did not observe $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ presumably because acid was present. They reported that ethylene glycol (and propylene glycol) gave "a triplet, similar to that from methanol, superimposed on rather ill-defined lines." They suggested that reactions of radicals derived from the glycol may have included C-C bond cleavage to give $\dot{\text{C}}\text{H}_2\text{OH}$. However, our measurements of this spectrum indicated that it was not $\dot{\text{C}}\text{H}_2\text{OH}$ since neither the hyperfine interaction nor the g value

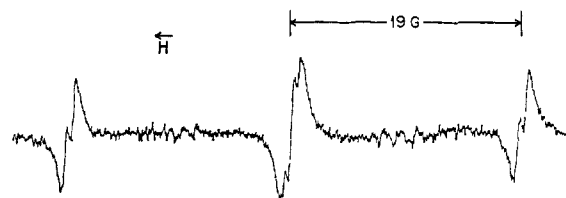
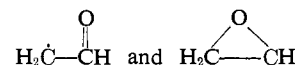


Figure 4. The spectrum obtained by photolysis of a solution containing equal volumes of ethylene glycol and water, 1% H_2O_2 , and 5 ml of concentrated H_2SO_4 /l. of solution and at -13° .

agreed closely. In order to settle this point more surely, an experiment was carried out in which the triplet and $\dot{\text{C}}\text{H}_2\text{OH}$ were seen in the same solution. The first part of the experiment was the photolysis of a solution containing equal volumes of ethylene glycol and water, 5 ml of concentrated HCl /l. of solution, and 1% H_2O_2 . This experiment, which was carried out at -10° , gave a strong triplet, and as indicated later, there were components partially resolved. The second part of the experiment was the addition of methyl alcohol to make the solution 20% in CH_3OH . Photolysis gave the above triplet and a distinct spectrum of $\dot{\text{C}}\text{H}_2\text{OH}$. The hydroxyl proton splitting of the $\dot{\text{C}}\text{H}_2\text{OH}$ was well resolved, since the acid concentration was not high enough⁴ for its elimination by exchange. This left no doubt that the triplet was not from $\dot{\text{C}}\text{H}_2\text{OH}$.

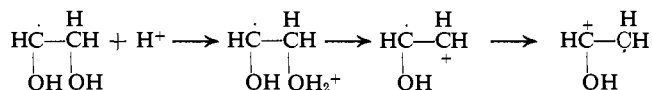
The lines of the triplet start to split into components at lower temperatures as indicated for -13° in Figure 4. The over-all splittings clearly come from two strongly coupled protons. The splitting of the outermost lines indicate there is a third very weakly coupled proton. The structure of the central line suggests that the pair of strongly coupled protons are not quite equivalent. With this interpretation, we find with less than usual accuracy three protons with hyperfine couplings of 19.2, 18.7, and 0.5 gauss and a g value of 2.0046. These measurements were made at -10.5° on a solution containing equal volumes of ethylene glycol and water, 5 ml of concentrated H_2SO_4 /l., and 1% of H_2O_2 . Reasonable arguments can be advanced that these parameters describe either of the following isomeric radicals.



We prefer the aldehyde structure because of the similarity of the parameters to those for $\dot{\text{C}}\text{H}_2\text{COCH}_3$ measured in acetone solution⁴ at -49.5° . The pair of CH_2 hydrogens of $\dot{\text{C}}\text{H}_2\text{COCH}_3$ were inequivalent with couplings of 19.95 and 19.48 gauss, and the g value was 2.00443. The small coupling of 0.27 gauss measured for the CH_3 protons of $\dot{\text{C}}\text{H}_2\text{COCH}_3$ is good assurance that the radical was not a ring structure (like propylene oxide missing a hydrogen in the 2 position), since a much larger coupling for the CH_3 hydrogens would be expected from the ring structure. The similarity of the g values seems significant. They are characteristically higher than those found² for alcohols and the value of 2.00314 found⁴ for the ether $\text{CH}_3\dot{\text{C}}\text{HOC}_2\text{H}_5$. The slight inequivalence of the pair of hydrogens at reduced temperatures appears reasonable for the aldehyde form of $\dot{\text{C}}\text{H}_2\text{CHO}$, since all atoms are probably coplanar in the most stable arrangement. Rotation

about the C-C bond is therefore probably restricted. The unpaired electron is in the π p orbital of the $\dot{\text{C}}\text{H}_2$ carbon most of the time as indicated by the large $\dot{\text{C}}\text{H}_2$ proton couplings. The very small coupling of the unique hydrogen two bonds away is reasonable, since this proton prefers to be in a plane normal to the p orbital. The ring structure cannot be completely dismissed since a small coupling was found⁷ for the unique hydrogen of the cyclopropyl radical and the reasons advanced could be the same in the two cases. Moreover, these reasons would admit to an inequivalence in the strongly coupled protons.

A mechanism⁸ for forming $\dot{\text{C}}\text{H}_2\text{CHO}$ that would be dependent upon the presence of acid involves carbonium ion intermediates and has features in common with the pinacol transformation. The initial step would be the abstraction of hydrogen by OH to give the radical observed in the absence of acid followed by



The final product would lose a hydrogen ion to give either an aldehyde group or ring closure. If the analogy to pinacol were strictly applicable, it would be the aldehyde group that formed. We have considered a variation of the above mechanism where the hydrogen ion adds to the other OH group in the first step, but this leads to an intermediate that seems unreasonable, a carbonium ion radical which would have only five electrons in the valence shell of one carbon atom.

Experiments were carried out with ethylene oxide and acetaldehyde to see if the above radical could be prepared by another method. The experiments were unsuccessful. Solutions of ethylene oxide in water and in *t*-butyl alcohol with added H_2O_2 were photolyzed, but no signals were obtained. When a small amount of acid was added to the aqueous solution poorly defined lines that were weak and broad appeared, but they did not correspond to the above radical. A solution of ethylene oxide in acetone (no H_2O_2) was also photolyzed since acetone often abstracts protons.⁴ Nice spectra were obtained, but they were just those found in the photolysis of pure acetone. A variety of solutions containing acetaldehyde were photolyzed, and although spectra were obtained, which will be described in a later paper, none correspond to the radical of interest. From the work on acetaldehyde it became evident that an important test was to see if the effects brought about by acid were reversible. The experiments with ethylene glycol were reversible. A solution containing equal volumes of ethylene glycol and water

(7) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(8) We thank C. J. Collins and V. F. Raaen for helpful discussion on this point.

and 1% H_2O_2 was found to be somewhat acid with a pH of about 5 as measured with a glass electrode. Photolysis gave $\dot{\text{C}}\text{HOHCH}_2\text{OH}$. Addition of 1 ml of concentrated H_2SO_4 /l. of solution dropped the pH to 1.8 which was more than adequate to bring in the triplet spectrum. Titrating with KOH solution to a pH of 5.3 restored the original spectrum, and continuing to a pH of 8 brought about no further change. When the titration was continued to a pH of 9.3 the spectrum of $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ disappeared once again, and in its place were several broad lines of unknown origin.

Summary

It has already been pointed out² that the g value of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$, 2.00247, is hydrocarbon-like in value and characteristically lower than g values of radicals formed by abstracting an α hydrogen from an alcohol. The g values found for $(\text{CH}_3)_2(\dot{\text{C}}\text{H}_2)\text{COH}$ and $\text{CH}_3-(\dot{\text{C}}\text{H}_2)\text{CHOH}$, 2.00241 and 2.00236, respectively, were also hydrocarbon-like in value as expected. The uniform trend of g values in simple aliphatic compounds containing oxygen makes them very useful in corroborating the assignment of spectra. For example, the g value of 2.0046 for the triplet formed from acidified aqueous ethylene glycol indicated at once that the radical was likely not a hydrocarbon nor a simple alcohol. The similarity of the value to that for the ketone $\dot{\text{C}}\text{H}_2\text{COCH}_3$, 2.00443, lent support to the identification of the radical as the aldehyde $\dot{\text{C}}\text{H}_2\text{CHO}$. At this time we can only guess that the g value of the ring form of $\dot{\text{C}}\text{H}_2\text{CHO}$ would be similar to those for ethers; for example, near the value of 2.00314 for $\text{CH}_3\dot{\text{C}}\text{HOC}_2\text{H}_5$. As more g values are measured with high accuracy they will probably be of increasing importance in corroborating assignments.

The abstraction of β hydrogens from *t*-butyl, isopropyl, and ethyl alcohols was greatly enhanced by the addition of water. The results for isopropyl and *t*-butyl alcohols became much more comparable to that reported in rapid-mixing experiments,³ although the spectrum from isopropyl alcohol by photolysis was much better resolved. The addition of acid generally improved signal strength, but, as explained, this could largely be a result of rapid exchange of the hydroxyl proton. Unlike rapid-mixing experiments the radicals formed by addition of OH to the double bond of allyl alcohol were not observed. Even in the presence of considerable water and acid the primary process was abstraction of an α hydrogen. Whereas photolysis of ethylene glycol containing H_2O_2 gave primarily a spectrum of $\dot{\text{C}}\text{HOHCH}_2\text{OH}$, the addition of water and acid caused this spectrum to disappear and a new one to form making the results much more comparable to the rapid-mixing experiments.