Photochemical Formation of Free Radicals from Olefinic and Acetylenic Compounds in the Frozen State as Studied by Electron Spin Resonance¹

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Electron spin resonance studies of ultraviolet-irradiated propargyl alcohol, allene, allyl chloride, 1,3-dichloropropene-1, 2,3-dichloropropene-1, 1-butyn-3-ol, methylallene, 2-chlorobutene-2, 1-chlorobutene-1, and 2methyl-3-butyn-2-ol have been made at 77°K. All of the three-carbon compounds gave allenyl free radical; all of the four-carbon compounds gave methylallenyl free radical. For the propargylic alcohols and allene hydrocarbons, these radicals originate from cleavage of the carbon-oxygen bond or carbon-hydrogen bond in the photochemical primary process. For the chloroolefins, the mechanism proposed is molecular detachment to form an allenic or acetylenic compound in the primary process; subsequently, with absorption of light, detachment of an atom yields the radical. As the temperature of previously irradiated propargyl alcohol or 1butyn-3-ol was raised, hydroxyallenyl or hydroxymethylallenyl radical attributed to α -hydrogen atom abstraction by hydroxyl radicals, formed in the primary process, was formed. These hydroxy radicals were also formed in solutions of the alcohols containing hydrogen peroxide on irradiation with light of wave length greater than 2800 Å., where only OH radicals are formed in the primary process. 2-Methyl-3-butyn-2-ol gave free methyl and $R\dot{C}H_2$, probably by primary processes.

Introduction

Recently we have reported some electron spin resonance studies of ultraviolet-irradiated allylic alcohols and solutions of hydrogen peroxide in allylic alcohols in the frozen state.² Allylic radicals were obtained from primary cleavage of the carbon-oxygen bond or from secondary reaction by abstraction of α -hydrogen atoms by hydroxyl radicals.

We had also studied ultraviolet-irradiated propargyl alcohol, which we expected would yield allenyl radical, and allyl chloride, which we expected would yield allyl radical. The e.s.r. spectra obtained for these two compounds were, however, almost identical. Our interest in this observation has led us to the investigation reported herein of some propargylic alcohols, allene hydrocarbons, and haloolefins.

Experimental

Materials and Preparation of Samples. Hydrogen peroxide (90%, Becco Chemical Division) was used without further purification. Propargyl alcohol and 2-methyl-3-butyn-2-ol (Eastman Practical), allene (Matheson), allyl chloride (Eastman White Label), 1,3-dichloropropene-1 and 2,3-dichloropropene-1 (Columbia Organic Chemicals), methylallene, 2-chlorobutene-2, 1-chlorobutene-1, and 2-chlorobutene-1 (K and K Laboratories), and 1-butyn-3-ol (synthesized by Dr. W. E. Thiessen) were purified by fractional distillation. Samples which contained hydrogen peroxide were prepared by adding 5 mg. of peroxide to 1 ml. of solvent. The samples were placed in 4-mm. quartz sample tubes, degassed by several freeze-pump-thaw cycles, and sealed while frozen with liquid nitrogen.

Irradiations and Spectrometer. Irradiations and observations were carried out either at a fixed temperature of 77 °K. by keeping the sample tube in a Varian liquid nitrogen quartz dewar insert or at temperatures above this by keeping the sample tube in a Varian variabletemperature quartz dewar insert. For this operation the temperature was maintained by dry nitrogen gas cooled by passage through a heat exchanger in liquid nitrogen. Temperature measurements $(\pm 2^{\circ})$ were made by a thermocouple.

In most of the experiments the light used was emitted from a low-pressure mercury resonance arc housed in Vycor. The transmitted light was chiefly 2537 Å. as Vycor is opaque to 1849-Å. light. For some experiments where solutions of hydrogen peroxide were used, a high-pressure mercury arc was used. The emitted light was filtered through Pyrex 0-53 glass which eliminated radiation shorter than 2800 Å.

The spectrometer was a Varian 4501 X-band electron paramagnetic resonance spectrometer with 100-kc. field modulation. Spectra were taken as first derivatives. Calibration of the scanning rates, gauss per minute, was made with peroxylamine disulfonate.

Results and Discussion

Allenyl Radical. Spectra resulting from the irradiation of allene, propargyl alcohol, allyl chloride, and 1,3dichloropropane with 2537-Å. radiation at 77°K. are shown in Figure 1. The spectrum obtained from 2,3-dichloropropene-1, not shown, was virtually identical with that obtained from 1,3-dichloropropene. The spectra shown were all obtained at the irradiation temperature (77°K.).

The spectra obtained from propargyl alcohol, allyl chloride, and 1,3-dichloropropene are almost identical; that from allene is very similar. This spectrum can be attributed to the allenyl radical

 $CH \equiv C - \dot{C}H_2$ $\dot{C}H = C = CH_2$

In Figure 2 the integrated absorption curves for propargyl alcohol and for allene, constructed from the derivative representations of Figure 1, are shown. For propargyl alcohol the intensity ratios taken from the peak heights are 1:2.9:2.7:1.2; for allene the ratios

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K. A. Maas and D. H. Volman, *Trans. Faraday Soc.*, 60, 1202 (1964).



Figure 1. E.s.r. spectra of compounds giving the allenyl radical on irradiation at 2537 Å. and 77°K. (spectra recorded at 77°K.).

are 1:2.3:2.2:0.8. Although the four peaks and the relative intensities are suggestive of equivalent interaction with three protons, this does not appear to be the case. The peak-to-peak separations are 18.0, 14.0, and 17.8 gauss for the spectrum from propargyl alcohol; for the allene spectrum, peak-to-peak separations are 17.6, 14.0, and 17.8 gauss. For equivalent protons, the spacings would be expected to be more nearly equal.

The unpaired spin densities on the terminal carbon atoms are not expected to be the same for the unsymmetrical canonical structures of the allenyl radical. Therefore, it is likely that the coupling constants for the CH₂ group protons differ from that of the CH proton. With coupling constants of 17.8 and 13.8 gauss assigned to the CH₂ and CH protons, the spectrum has been reconstructed as shown in the theoretical curve of Figure 2. The vertical lines represent the resonance spacings and intensities, 1:1:2:2:1:1, based on the assigned coupling constants. The line shape used in the reconstruction is that of the first half of the lowfield line of the experimental allene spectrum. This part is least affected by asymmetry and overlap. For intensity 2 lines, the ordinate was doubled whereas the field increment was the same as for the unity intensity lines.

The agreement between the reconstructed spectrum and the experimental spectra is reasonably good considering the inherent difficulty in choosing a proper line shape applicable to all of the lines. The peak intensity ratios are 1:2.3:2.3:1, which compare favorably with both the propargyl alcohol and allene experimental values.

The proton hyperfine coupling constants are consistent with the relationship of McConnell and Chesnut, $\alpha = Q\rho$, for π -radicals, where Q is about 23



Figure 2. Integrated experimental absorption spectra and calculated absorption curve for allenyl radical.

gauss and ρ is the unpaired spin density. Spin densities of about 0.8 and 0.6 are then obtained for the CH₂ and CH carbon atoms, respectively. These are reasonable values in view of the unsymmetrical canonical structures for the allenyl radical and the existence of negative spin density on the central carbon atom. It may be observed that the free energy of formation, $\Delta F_{\rm f}^{\circ}_{298}$, is about 2 kcal. more negative for propyne than for allene. This would correlate with greater stability for $CH = C - \dot{C}H_2$ than for $\dot{C}H = C - CH_2$ and, hence, a larger unpaired spin density for the CH₂ group carbon.

Spectra from the allenvl radical have previously been reported by Poole and Anderson,⁴ for the product from the ultraviolet irradiation of propyne at 77°K., and by Fessenden and Schuler,⁵ in a note added in proof for preliminary work on electron irradiation of a solution of allene in propane. (The temperature for this experiment was not given, but, presumably, the solution was in the liquid state at about -180° .) The spectrum reported by Poole and Anderson was a quartet attributed to coupling with three equivalent protons with a hyperfine interval of 32 gauss. Fessenden and Schuler report a six-line spectrum attributed to 18.9gauss coupling with the two CH₂ protons and 12.6-gauss coupling with the CH proton. Our results are in general agreement with those of Fessenden and Schuler after allowance is made for the broad lines obtained in our experiments, the rigid matrix, compared to the narrow lines obtainable in liquid solution. The 32gauss spacing reported by Poole and Anderson is, inexplicably, about twice that expected, as found by us or by Fessenden and Schuler.

Cleavage of the carbon-oxygen bond of propargyl alcohol or of a carbon-hydrogen bond of allene in the photochemical primary process would yield the allenyl radical. These are, moreover, the expected primary processes. The formation of allenyl radical from allyl

⁽³⁾ H. M. McConnell and D. B. Chesnut, J. Chem. Phys., 28, 107 (1958). (4) C. P. Poole, Jr., and R. S. Anderson, *ibid.*, **31**, 346 (1959).

⁽⁵⁾ R. W. Fessenden and R. H. Schuler, ibid., 39, 2147 (1963).

chloride, 2,3-dichloropropene-1, and 1,3-dichloropropene is obviously more complicated. These molecules must each lose three atoms in order to yield the allenyl radical. Very little is known of the photochemistry of the haloethylenes. There is, however, good evidence that the primary process in 1,2-dichloroethylene is the detachment of hydrogen chloride or two chlorine atoms.⁶ Molecular detachment of HCl from allyl chloride would yield allene; detachment of HCl, Cl₂, or two Cl atoms from the dichloro compounds would yield chloroallene or allene. Absorption of light by allene or chloroallene would then yield allenyl radical by primary process. At this time the only evidence we have for the formation of a molecular intermediate is that comparatively prolonged irradiation is necessary to produce the free-radical spectrum.

Methylallenyl Radical. Irradiation of 1-butyn-3-ol, methylallene, 2-chlorobutene-2, 1-chlorobutene-1, and 2-chlorobutene-1 at 2537 Å. and 77°K. gave radicals whose spectra were almost identical. The spectra from two of the compounds, 1-butyn-3-ol and methylallene, are shown in Figure 3. These spectra can be attributed to the same radical, methylallenyl

HC=C-ĊH-CH₃ HĊ=C-CH-CH₃

In Figure 4, the integrated absorption curve for 1butyn-3-ol constructed from the derivative curve of Figure 3 is shown. The curve indicates six absorption maxima with a total spread of 85 gauss, an average peak-to-peak separation of 17.0 gauss, and intensity ratios of 1:4.3:8.1:8.5:5.6:1.4, not far different from the theoretical 1:5:10:10:5:1 expected for five equivalent protons. In view of the discussion of the allenyl radical, it is hardly likely that the coupling constants for the total of five protons, all of which should contribute to the spectrum, are equivalent. It is, however, expected that the three methyl protons would have the same coupling constants. If the other two protons have different coupling constants, and different from each other, a 16-line spectrum could result; if the other two protons have very similar coupling constants, a 12-line spectrum could result. In either case a conformance to the curve of Figure 4 would be likely if the coupling constants were not more than a few gauss apart. For the 16-line spectrum it would be expected that there would be groupings of 1, 3, 4, 4, 3, and 1 lines; for the 12-line spectrum the groupings would be 1, 2, 3, 3, 2, and 1 lines. The additive intensities would, of course, approximate the theoretical values. On the basis of our spectrum, it is not possible to make a choice among the various possibilities. The coupling constants would be expected to be not too far different and, perhaps, even closer together than in the allenyl radical.

The mechanism of formation of methylallenyl radical from its precursors must be the same as that for the formation of allenyl radicals from its precursors. Cleavage of the C–O bond in the alcohol or the C–H bond in the hydrocarbon would yield the radical in the primary process. From the other compounds, molecular elimination of HCl followed by cleavage of the C–H bond on further absorption of light would yield the radical.

Hydroxyallenyl and Hydroxymethylallenyl Radicals.

(6) M. H. J. Wijnen, J. Am. Chem. Soc., 83, 4109 (1961).



Figure 3. E.s.r. spectra of compounds giving the methylallenyl radical on irradiation at 2537 Å. and 77° K. (spectra recorded at 77° K.).



Figure 4. Integrated experimental absorption spectrum for irradiated 1-butyn-3-ol.

The electron spin resonance spectra of hydroxyallylic^{2,7} radicals have been observed from the reaction of hydroxyl radical with various allylic alcohols. The analogous reaction, abstraction of an α -hydrogen atom by hydroxyl, with propargylic alcohols would result in the formation of hydroxyallenic radicals. Evidence for the formation of hydroxyallenyl

and hydroxymethylallenyl

radicals has been obtained in this study.

Propargyl alcohol irradiated at 2537 Å. and 77°K. gave the spectrum shown in Figure 1. When the irradiated sample was warmed to 147°K., the spectrum changed to that shown in Figure 5. A solution of hydrogen peroxide, 5 mg., in propargyl alcohol, 1 ml., irradiated with light from a high-pressure mercury arc through a Pyrex filter, $\lambda > 2800$ Å., and warmed to 142°K. gave the spectrum shown in Figure 5. Similar experiments were carried out with 1-butyn-3-ol and the

(7) J. F. Gibson, D. J. E. Ingram, M. C. R. Symons, and M. G. Townsend, Trans. Faraday Soc., 53, 914 (1957).



Figure 5. E.s.r. spectra of systems giving hydroxyallenyl radical and hydroxymethylallenyl radical (irradiations carried out at 77 °K.; mixed samples irradiated at $\lambda > 2800$ Å.).

results are also shown in Figure 5. At 160° K. the spectrum was disappearing with time, and the sample was therefore cooled to 120° K. before the spectrum marked 160° K. was recorded.

At $\lambda > 2800$ Å, light absorption would be limited to H_2O_2 in the mixed samples. The spectra in the mixed samples must, therefore, come from the products of the reaction of hydroxyl radical, the primary product of H_2O_2 photolysis, with the alcohol. As may be clearly seen in the propargyl alcohol system, the spectra are the same for the experiments with and without added peroxide. Both spectra may then be attributed to the reaction of hydroxyl with propargyl alcohol, hydroxyl radicals being formed in the primary cleavage of the carbon-oxygen bond at 2537 Å. when peroxide is absent. We have advanced this argument previously in considering free radicals formed from allylic alcohols.²

Two possible reactions of hydroxyl radical with propargyl alcohol may be considered: addition to the triple bond or abstraction of an α -hydrogen atom. Addition of hydroxyl in either the β - or γ -position would result in a vinylic radical. The coupling constants⁵ for either vinylic radical would result in a much wider spectrum than the one obtained. The spectrum, therefore, may be accounted for by the hydroxyallenyl radical which would result from α -hydrogen atom abstraction. This mechanism has been proposed by Dixon and Norman⁸ for the reaction of hydroxyl radicals with propargyl alcohol in aqueous solution at

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



Figure 6. E.s.r. spectra of 2-methyl-3-butyn-2-ol irradiated at 2537 Å, and 77 $^{\circ}$ K., showing methyl and RCH₂ radicals.

room temperature. The integrated spectrum gave a three-peak profile with equal spacings of 15 gauss, as would be expected from coupling with two nearly equivalent protons. The relative intensities were 1:1.5:0.9. It is possible that the doublet splitting of the lines may be attributed to the hydroxyl proton. Symons⁹ has calculated that configurational interaction from this proton could result in a splitting of as much as 7.9 gauss. In view of the fractional unpaired spin density in this radical, the splittings of about 4 gauss for the doublets appear reasonable.

For irradiated 1-butyn-3-ol, the effects of warming the sample are analogous to those observed for propargyl alcohol. The six-line pattern is changed to a five-line pattern which would result from α -hydrogen atom abstraction by hydroxyl radical to yield the hydroxymethylallenyl radical. From the integrated absorption curve for this spectrum, we have calculated a total spread for five absorption maxima of 66 gauss, average spacing of 17 gauss, and intensity ratios of 1:3.8:4.3:2.7:0.7, in reasonable conformance with theory for four equivalent protons. With peroxide present, the spectrum obtained is not the almost duplicate as was found for propargyl alcohol. This poorly resolved spectrum does, however, have five lines with an average separation of 17 gauss, in agreement with the proposed mechanism.

Methyl Radical from Irradiation of 2-Methyl-3butyn-2-ol. This alcohol does not have an α -hydrogen atom and is the propargylic counterpart of the allylic alcohol, 2-hydroxy-2-methyl-3-butene, which we have studied earlier.² The results obtained, as shown in Figure 6, are completely analogous to those we have reported for the olefin. Methyl radical was clearly formed as the marked peak positions at 77°K. indicate. The average peak separation was 23 gauss and

(9) M. C. R. Symons, ibid., 277 (1959).

the intensities were 1:3.0:3.0:1, in conformance with theory for free methyl radical. When the sample was warmed to 112°K., the four-line spectrum was considerably diminished while the superimposed three-line spectrum, marked on the 112°K. spectrum, did not change appreciably. The total spread for the three peaks is 46 gauss, or 23 gauss average, which could come from two equivalent protons after detachment of an hydrogen atom from a methyl group. As both the four-line and three-line spectra seem to be present at 77°K., it is probable that methyl radical is formed by carbon-carbon bond cleavage and that RCH₂ radical is formed by carbon-hydrogen bond cleavage in the photochemical primary process.

Organic Ions in the Gas Phase. XVI. Isomeric C₂H₂O⁺ Ions from Benzoic Acid Seymour Meyerson and J. L. Corbin

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Deuterium labeling reveals that 18% of the $C_1H_5O^+$ ions in the mass spectrum of benzoic acid arises by loss of a hydroxyl group containing hydrogen from the ortho position. The product is chemically distinct from the isomeric and more abundant benzoylium ion. It is formulated as the conjugate acid of the ortho isomer of a short-lived species recently reported among the products of flash photolysis of benzenediazonium-4-carboxylate.

The literature of mass spectrometry is replete with examples of ionic species the identities of which seem, at first glance, so obvious as to scarcely merit attention but upon close scrutiny are found to be quite different from what they seem.¹ A curious example of such a species occurs in the mass spectrum of benzoic acid.

The spectra of aromatic acids are characterized by intense peaks at the parent mass less 17 and less 45 units, corresponding to the ArCO⁺ and Ar⁺ ions.²⁻⁴ Metastable peaks establish that the latter product arises, at least in part, by secondary loss of CO from ArCO+ ion.⁵ The data thus define the reaction path

The neutral products lost in the reaction have been assumed^{2,3} to consist solely of the original OH and CO groups. However, the spectrum of a sample of benzoic acid-2,3- d_2^6 suggested that about 9% of the parent-lesshydroxyl ions had lost a deuterium atom rather than protium. The possibility that part of the deuterium in the labeled acid was in the carboxyl group rather than in the ring was ruled out because the isotopic analysis of the acid was virtually identical with that of the toluene-2,3- d_2 from which it had been made.⁷ The apparent incorporation of a ring hydrogen atom into the hydroxyl group lost prompted us to prepare and to study the mass spectra of benzoic acids labeled with a single deuterium in the ortho, meta, and para positions.

Experimental

The singly labeled acids were prepared from Eastman Kodak White Label bromotoluenes. These were converted to Grignard reagents and hydrolyzed with deuterium oxide; the resulting toluenes were oxidized to the acids with potassium permanganate. Chemical purity of the toluenes and benzoic acids was established by the mass spectra. Isotopic compositions, estimated from low-voltage spectra,⁸ are shown in Table I.

Mass spectra of the acids were measured with 70-v. electrons on a modified⁹ Consolidated Model 21-103c instrument with the inlet system at 250°.

Results and Discussion

Table II shows partial spectra of benzoic acids unlabeled, -2-d, -3-d, -4-d, and $-2,3-d_2$, corrected both for naturally occurring heavy isotopes and for isotopic impurities. An attempt to remove the d_1 impurity from the d_2 spectrum as the 2-d species left negative residues at masses 104 and 105, implying that the impurity must be, at least in large part, a species other than 2-d. In the spectrum shown, the d_1 impurity therefore was removed as the 3-d species. Table II lists metastable peaks and the transitions denoted by them.

Sequential Loss of OH and CO. The most abundant ions and the associated metastable peaks correspond to sequential loss of OH and CO. But both normal and metastable peaks show loss of OD as well as of OH in the 2-d and $2,3-d_2$ spectra. Moreover, the isotopic

 ⁽¹⁾ For several such instances, see H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Aca-demic Press Inc., New York, N. Y., 1963, p. 453.
(2) F. W. McLafferty and R. S. Gohlke, Anal. Chem., 31, 2076

^{(1959).}

⁽³⁾ T. Aczel and H. E. Lumpkin, ibid., 33, 386 (1961).

⁽⁴⁾ Products of competing decomposition paths important in the spectra of ortho-substituted acids are ignored here as irrelevant to the present system.

⁽⁵⁾ Unpublished spectra, this laboratory.

⁽⁶⁾ For the gift of this material, we are indebted to L. C. Leitch, of the National Research Council of Canada. See R. N. Renaud, D. Kovachic, and L. C. Leitch, *Can. J. Chem.*, **39**, 21 (1961).

⁽⁷⁾ Our own isotopic analysis of the toluene- d_2 (see S. Meyerson, J. Am. Chem. Soc., 85, 3340 (1963)) agreed closely with that reported in ref. 6.

⁽⁸⁾ D. P. Stevenson and C. D. Wagner, J. Am. Chem. Soc., 72, 5612 (1950).

⁽⁹⁾ H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moeller, 7th Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, Los Angeles, Calif., 1959.