

It is apparent that the simplicity and versatility of the flowing afterglow technique make it a very useful technique for the study of gas-phase organic ion-molecule reactions. At the present time, the most serious drawbacks for the study of organic reactions are that rate constants are obtainable only when the reactant is a gas at atmospheric pressure and that for qualitative measurements the organic compounds used must have a fairly high vapor pressure at the system pressure (ca.

0.4 Torr). These limitations, however, still allow the study of a large number of organic reactions.

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Electron Spin Resonance Spectra of Radicals Produced by Hydrogen and Deuterium Bombardment of Unsaturated Organic Compounds at 77°K

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Abstract: The radicals produced by the interaction of unsaturated hydrocarbons with hydrogen atoms at 77°K have been studied by electron spin resonance (esr). The hydrogen atom adds directly to the double bond of ethylene, 1,3-butadiene, and benzene to produce the ethyl, 2-butenyl, and cyclohexadienyl radicals, respectively. In the case of the interaction of hydrogen atoms with 1-butyne and 1,2-butadiene, the methylallenyl radical was observed in each case. On bombardment of 1,4-cyclohexadiene and propyne with hydrogen atoms the cyclohexadienyl and allenyl radicals were observed. These last four reactions can be explained by assuming an addition reaction of hydrogen with the compound. The radical produced immediately abstracts a hydrogen atom from the parent compound to yield the observed stable radical. For the 1,2-butadiene-hydrogen interaction, such a mechanism accounts for the esr spectrum and for the 2-butyne and 2-butene observed by Klein and Scheer¹ in their analysis of the products of this reaction after warming to room temperature. The formation of 2-butene and 2-butyne can also be explained, respectively, by a double addition and an addition and abstraction reaction of hydrogen with 1,2-butadiene. In this case the radical observed by esr would be explained by a single abstraction reaction.

In recent years considerable interest has arisen concerning the interaction of hydrogen atoms with unsaturated hydrocarbons held at or near liquid nitrogen temperatures, as in the work of Klein and Scheer.²⁻⁸ The number of reactions initiated at this temperature is reduced considerably when compared with the same reaction at ambient temperatures. Klein and Scheer have used the gas chromatographic technique to study the reaction of these products after they have warmed to room temperature and from these data have inferred some of the low-temperature hydrogen-olefin reactions. In numerous cases they have found that the radical disappears by disproportionation and dimerization reactions when the radicals are free to migrate as the compound is warmed. For some matrices, particularly propane, the radical is able to migrate even at 77°K. In most of these reactions the initial step is the hydrogen addition to the double bond.

In this experiment we have attempted to observe by esr at 77°K the radicals produced in this initial reaction for both hydrogen and deuterium atom bombardment. Chachaty and Schmidt⁹ and Forchioni and Chachaty¹⁰ also carried out this procedure for compounds such as allyl alcohol, ethanol, isopropyl alcohol, and 2-chloroethanol. Others have performed these studies with solids at ambient temperatures.¹¹⁻¹³ We have chosen to examine the interaction of hydrogen atoms with ethylene, 1,2-butadiene, 1,3-butadiene, propyne, 1-butyne, benzene, and 1,4-cyclohexadiene.

Experimental Section

The gases used without purification in these determinations included Matheson ethylene (99.5%), propyne (96%), 1,3-butadiene (99.5%), deuterium (98.0%), and hydrogen (99.9%). Three of the liquids used were 1,2-butadiene (95%), 1-butyne (99.7%), and 1,4-cyclohexadiene (99%), obtained from the Chemical Samples Co. The benzene used was Fisher ACS grade.

The experimental apparatus used is shown in Figure 1. It is similar to that used by Chachaty and Schmidt. The volume of the dewar and gas handling system with the main stopcock to the pump

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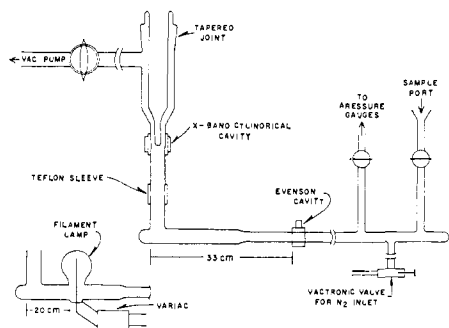


Figure 1. Experimental arrangements of apparatus for hydrogen atom bombardment. Lower left: tungsten assembly for generating hydrogen atoms.

closed is approximately 1 l. The system is pumped down to a pressure of 10^{-4} Torr without any liquid nitrogen in the cold trap. The main stopcock to the pump is closed and the gaseous sample is added to the system until the pressure increases to about 40 Torr. Liquid nitrogen is then added to the very tip of the cold finger and the sample collects as a solid at this point. When the pressure decreases to about 1 Torr the trap is completely filled with liquid nitrogen and the pump stopcock is then opened and the system is pumped down. The hydrogen or deuterium is introduced into the system through a Vactronic VVS-50-Q precision valve after passing through a liquid nitrogen trap for drying. The gas was dissociated in an Evenson cavity powered by a Raytheon microwave generator operating at approximately 2400 MHz. The sample was irradiated for periods that varied from a few seconds up to 15 min. The hydrogen was introduced at a pressure of 1 Torr at a flow rate of about 1.6 ml (STP)/sec.

One of the complications encountered in this experiment was the possibility of photolysis of the sample under study by the ultraviolet radiation generated in the discharge. In order to exclude as much of this light as possible, the discharge tube in Figure 1 was made of Pyrex as far as the Teflon sleeve connection, and a short extension to the tube was made at the 90° bend to minimize the reflection of light up the tube to the sample. An additional technique used was the replacement of the Raytheon discharge system by a heated tungsten filament as shown in Figure 1. This was also used to discriminate against possible impurity radicals that could be produced by the discharge. The filament assembly was made from a General Electric DFD 1000-W projection lamp, and the voltage to the lamp was controlled with a variable autotransformer. Using identical experimental conditions both methods produced adequate concentrations of hydrogen atoms that could be monitored by the esr spectrometer. The radicals produced at 77°K by the bombardment were monitored with a Varian X-4500 spectrometer using 100-KHz modulation. The cylindrical X-band cavity used in this work has a quality factor (Q) of about 6000. The cavity has a 1.9-cm access hole, and the collars for the top and bottom of cavity were made 2.5 cm thick. The cavity operated in the TE_{011} mode. The cylindrical part of the cavity was constructed from a Lucite block which was chemically coated with silver¹⁴ and then electroplated to a thickness of about 0.002 cm. In this way adequate modulation at the sample was obtained.

Results

The only observable radical produced by the hydrogen atom bombardment of ethylene was the well-known ethyl radical, and its spectrum is shown in Figure 2A. Only 8 of the 12 lines were observed. The measured splitting was 26.8 ± 0.5 G between the two strong components and 6.5 ± 0.5 G between the weak components. This leads to coupling constants of 26.8 and 20.3 G, which are in reasonable agreement with those of numerous other authors.¹⁵⁻¹⁹ Because of an-

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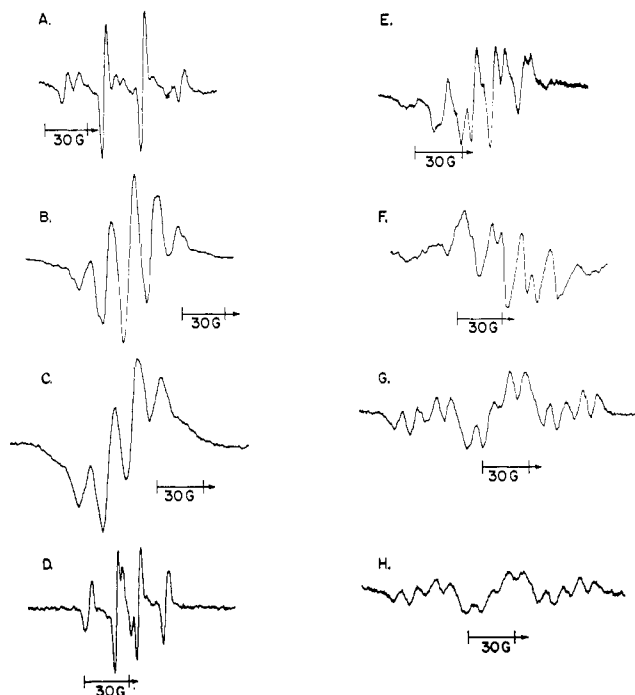


Figure 2. A, Ethyl radical spectrum; B, 2-butenyl radical spectrum; C, 2-butenyl- d_1 radical spectrum; D, allenyl radical spectrum; E, methylallenyl radical produced by the 1-butyne-hydrogen reaction; F, methylallenyl radical produced by the 1,2-butadiene-hydrogen reaction; G, cyclohexadienyl radical produced by the benzene-hydrogen reaction; H, cyclohexadienyl radical produced by the 1,4-cyclohexadiene-hydrogen reaction. All spectra recorded at 77°K .

isotropic effects intensity ratios were difficult to estimate.

The H atom reaction with 1,3-butadiene gave the five-line spectrum shown in Figure 2B. The splitting between the components was measured to be 16 ± 0.8 G. This spectrum is produced by the 2-butenyl radical, which can be represented by the two resonating structures, $\text{H}_2\text{C}=\dot{\text{C}}\text{HCH}_2$ and $\text{H}_2\dot{\text{C}}\text{CH}=\text{CHCH}_2$. The spectrum represents the interaction of six equivalent protons with the unpaired electron. The six protons are made up of three α and three β protons equally coupled to the electron. This interaction theoretically should produce a spectrum of seven lines of intensity 1:6:15:20:15:6:1. The intensity ratios of the spectrum in Figure 2B were measured by using a DuPont 310 curve resolver, modified to generate first derivative line shapes. These intensities were 1:3:4:2.9:1.1. This is in reasonable agreement with the central five theoretical intensities. Two wing lines of about $1/8$ intensity could have been superimposed at the extremities, which would not have greatly altered the spectrum; hence the presence of these lines could not be positively established. These same results were found by Maas and Volman²⁰ who identified the species as the 2-butenyl radical. Poole and Anderson²¹ reported a splitting of 21 G for a seven- or nine-line spectrum of a radical produced by the uv irradiation

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(19) P. J. Sullivan and W. S. Koski, *J. Amer. Chem. Soc.*, **86**, 159 (1964).

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

(21) C. P. Poole, Jr., and R. S. Anderson, *J. Chem. Phys.*, **31**, 346 (1959).

of 2-pentene. This was identified as either the 2-butenyl or the 1-methyl-2-butenyl radical. If it is the former then the difference between these results and those of Maas and Volman and this report are inexplicable.

The bombardment of 1,3-butadiene with D atoms at 77°K produced the spectrum of Figure 2C which was assigned to the 2-butenyl- d_1 radical whose structures are $\text{H}_2\text{C}=\dot{\text{C}}\text{HCH}_2\text{D}$ and $\text{H}_2\dot{\text{C}}\text{H}=\text{CHCH}_2\text{D}$. In this case the main hyperfine splitting is produced by the interaction of five equivalent protons with the free electron (three α and two β protons). This would give a spectrum of six lines of intensity 1:5:10:10:5:1. The splitting due to D is much smaller and only broadens the lines. The estimated relative intensities from Figure 2C are 1:5:9.2:9.5:5:1. This is in reasonable agreement with the theoretical spectrum. Again the weak broad satellites could be simulated on the curve resolver and only produced shoulders on the four central lines. The measured splittings were 16 ± 0.8 G.

For propyne at 77°K, the H atoms add to the triple bond to form the $\text{CH}_2=\dot{\text{C}}\text{CH}_3$ radical. This radical then abstracts an H atom from another matrix molecule to form the allenyl radical, which can be represented by the two structures $\text{HC}\equiv\dot{\text{C}}\text{H}_2$ and $\text{H}\dot{\text{C}}=\text{C}=\text{CH}_2$. The four-line spectrum of this allenyl radical is shown in Figure 2D. This is the same spectrum that Volman, Maas, and Wolstenholme²² obtained for this radical at 77°K. In Figure 2D the peak-to-peak separations of the four lines are 18.0, 14.3, and 18.2 ± 0.8 G, and the intensity ratios were about 1:1.85:2:1.35. Poole and Anderson²¹ observed a four-line spectrum after the uv irradiation of propyne. They measured a splitting of 32 G and identified this species as the propynyl radical. There appears to be no explanation for the difference between these results and those reported by Volman, *et al.*, and us.

Figures 2E and 2F show the ten-line spectra produced by the bombardment of 1-butyne and 1,2-butadiene with H atoms at 77°K. A splitting of 12.5 ± 0.8 G was measured between the two strong central lines and 18.4 ± 0.8 G between the strong central line and the strong outer line. The spectrum in each case is characteristic of the methylallenyl radical and again agrees with the spectrum of Volman, *et al.*, for this radical. Here the methylallenyl radical is formed by a consecutive addition and abstraction mechanism as was characteristic of the allenyl radical in the case of propyne. The two resonating structures are $\text{H}\dot{\text{C}}=\text{C}=\text{CHCH}_3$ and $\text{HC}\equiv\dot{\text{C}}\text{HCH}_3$. The spectrum can be constructed by assuming a coupling of 18.4 G with four equivalent protons and 12.5 G with one proton. Such a spectrum would yield intensity ratios of 1:1:4:4:6:6:4:4:1:1. It is seen from the spectrum that hyperfine anisotropy distorts the line widths and shapes, and hence, accurate intensity ratios could not be found. Deuterium atom bombardment of both propyne and 1-butyne produced the same radicals as the hydrogen bombardment. This is consistent with the consecutive addition and abstraction reaction mechanism.

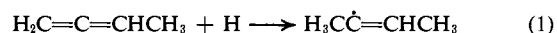
Benzene was bombarded with H atoms at 77°K and the resulting 12-line spectrum is shown in Figure 2G. The splitting between individual components was mea-

sured to be 10.6 ± 0.5 G and the splitting between the three groups of lines was 48 ± 0.5 G. This spectrum is characteristic of the cyclohexadienyl²³ radical, indicating an addition of a hydrogen atom to one of the double bonds of the benzene ring. Chachaty and Schmidt⁹ have observed this reaction. The intensity ratio of the central group to the two external groups of lines is about 2:1, indicating that there is probably no spectrum from any other radical present, as was observed by Ohnishi, *et al.* Upon irradiation of 1,4-cyclohexadiene with H atoms the same spectrum was obtained at 77°K (Figure 2H).

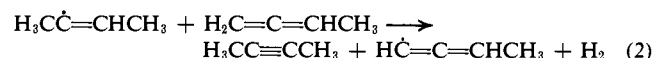
Ethylene, 1-butyne, propyne, and 1,2-butadiene were irradiated with H atoms using both the discharge and tungsten filament methods. The results were the same, using either method, indicating that ultraviolet radiation was probably not a significant problem. In the case of benzene, 1,4-cyclohexadiene, and 1,3-butadiene, only the discharge method was utilized.

Discussion

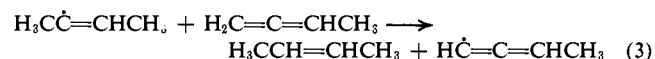
In the case of the addition of H atoms to ethylene, 1,3-butadiene, and benzene the reaction mechanism appears to be a simple addition of the free atom to the double bond. With the reaction involving propyne, 1,2-butadiene, 1-butyne, and 1,4-cyclohexadiene two mechanisms—an indirect and a direct abstraction—could account for the electron spin resonance results. The indirect mechanism was mentioned in the previous section and involves the addition of an H atom to a double or triple bond to form an intermediate unstable radical. This intermediate radical then abstracts a hydrogen atom from a parent matrix molecule to form a stable radical at 77°K. The indirect abstraction mechanism for 1,2-butadiene involves first a terminal addition reaction



followed by radical reaction with a parent matrix molecule



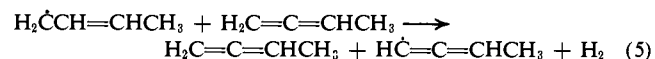
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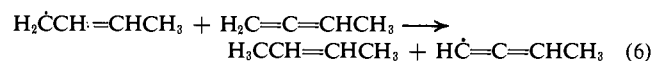
The reaction could proceed *via* an internal addition



followed by radical reaction with the parent matrix molecule



and



The direct abstraction is represented by



Starting with the products of the direct reaction indicated in eq 7, it would be extremely difficult to account for the stable products detected in the work of Klein and

(22) D. H. Volman, K. A. Maas, and J. Wolstenholme, *J. Amer. Chem. Soc.*, **87**, 3041 (1965).

(23) S. Ohnishi, T. Tanei, and I. Nitta, *J. Chem. Phys.*, **37**, 2402 (1962).

Sheer¹ on 1,2-butadiene. The indirect mechanism, on the other hand, fits their results quite well. In their work three of the major four carbon products were *trans*- and *cis*-2-butene and 2-butyne. It may be noted from eq 5 and 6 that for internal addition no 2-butyne is formed, which is contrary to their results. Hence it is possible that both internal and external addition take place, but it cannot be exclusively internal addition. Klein and Scheer claim that nonterminal addition does not occur.

An additional mechanism has been suggested²⁴ which would account for the formation of 2-butene and 2-butyne. After the initial addition reaction indicated in eq 1 the following addition and abstraction reactions take place.



and



The esr spectrum would be generated by reaction 7. Such a mechanism would require the immediate reaction of the $\text{H}_3\dot{\text{C}}\text{C}=\text{CHCH}_3$ radical with another hydrogen atom since this radical is not observed by esr. It would also mean that the reaction is not very specific as the hydrogen atom both adds and abstracts from both the parent molecule and the radical.

(24) The authors are indebted to Dr. Milton D. Scheer for this suggestion.

In the case of propyne an exactly analogous series of reactions can be postulated. The hydrogen addition takes place to form $\text{CH}_3\dot{\text{C}}=\text{CH}_2$. This radical abstracts from the parent compound, propyne, to yield the allenyl radical and either propylene or propyne and hydrogen. The same results are found from terminal or internal addition. Similar analyses can be applied to 1-butyne and 1,4-cyclohexadiene. However, for these three compounds we do not have any data on the resultant products when the compound is warmed to room temperature. Consequently, the esr spectra could be explained by the direct abstraction of H atoms from the initial compound or by the indirect method.

Conclusions

In the case of the addition reactions involving ethylene, 1,3-butadiene, and benzene, a simple addition of hydrogen atoms to a double bond appears to be sufficient to explain the results.

In the case of propyne, 1-butyne, 1,2-butadiene, and 1,4-cyclohexadiene the direct abstraction mechanism is enough to explain the esr spectra. However, for 1,2-butadiene the direct mechanism does not explain the results of Klein and Scheer, unless further abstraction and addition reactions take place between the radical and the hydrogen atom. The indirect mechanism does account for both phenomena. If either of these mechanisms is the correct one it indicates that the radical formed by direct addition, $\text{CH}_3\dot{\text{C}}=\text{CHCH}_3$, is very reactive and has a short lifetime at 77°K.

Fast Reaction Kinetics of Porphyrin Dimerization in Aqueous Solution¹

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Abstract: Temperature jump relaxation measurements were made on aqueous solutions and ethanol-water mixtures of the water-soluble porphyrin prepared by addition of four molecules of ethylenediamine to protoporphyrin IX. Measured relaxation times are of the order of magnitude of milliseconds and decrease slightly with pH in the range 3–7. Below pH 3, two different relaxation processes with different dependence on porphyrin concentration become apparent. From analysis of the kinetic data, confirmed by spectrophotometric and fluorometric studies, the phenomenon giving rise to the relaxation is found to be dimerization. At pH 6.0, 28°, in H₂O, the rate constant of dimerization is $7.8 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$. The reverse rate constant is 110 sec⁻¹. At lower pH, where the predominant porphyrin species contains three protons at its center, dimerization also occurs but at somewhat slower rate ($3.5 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$). In this case the rate increases with concentration (but not identity) of added salt, as for reactions between similarly charged ions. At still lower pH, where the predominant porphyrin species contains four protons at its center, simple dimerization apparently does not occur. Data are also given for dimerization equilibrium constants and rate constants for ethanol-water mixtures. All experiments were performed at several temperatures so that activation energies could be determined. These are found to be relatively small in all cases, indicating little energy barrier to dimerization. The fact that rates are considerably slower than diffusion controlled must indicate an unfavorable activation entropy resulting from necessary changes in water structure.

In earlier work,^{2–4} we have studied the insertion of metals into porphyrins. Such studies indicate that the

insertion reaction is not simple. In order to gain further insight into the steps of the reaction, temperature jump relaxation measurements were made on porphyrin

(1) Supported by a grant from the National Institutes of Health, U. S. Public Health Service.

(2) S. L. Baum and R. A. Plane, *J. Amer. Chem. Soc.*, **88**, 910 (1966).

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(4) T. P. Stein and R. A. Plane, *ibid.*, **91**, 607 (1969).