[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF RHODE ISLAND, KINGSTON, RHODE ISLAND, AND INSTRUMENT DIVISION, VARIAN ASSOCIATES, PALO ALTO, CALIFORNIA]

Low Temperature E.p.r. Studies of Free Radicals in the Ultraviolet Catalyzed Addition of Hydrogen Bromide to Olefins[1]

BY PAUL I. ABELL AND L. H. PIETTE

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The addition of bromine atoms from photolyzed hydrogen bromide to cyclopentene, cyclohexene, 2-butyne, 3-hexyne, *cis-trans*-2-butene, 3-hexene and vinylcyclohexane at 77°K. produces radicals which have been characterized by their electron paramagnetic resonance spectra. The spectra of the radicals are analyzed as to whether or not they are consistent with a "bridged" model for the bromoalkyl radical. The hyperfine interaction of the various hydrogens adjacent to the free electron is discussed. In general the symmetrical or bridged structures seem to offer the best interpretation of the spectra. Experiments with deuterium bromide verify the attack of the bromine atom as the initial event in the reaction.

Introduction

The addition of hydrogen bromide to olefins under non-polar conditions is one of the classical free radical reactions. Both Kharasch[2] and Hey[3] independently proposed a chain mechanism for the reaction.

$$\mathrm{HBr} \longrightarrow \mathrm{H}\cdot + \mathrm{Br}\cdot$$

$$\mathrm{Br}\cdot + \text{olefin} \longrightarrow \text{Bromoalkyl radical}$$

$$\text{Bromoalkyl radical} + \mathrm{HBr} \longrightarrow \text{Saturated bromide} + \mathrm{Br}\cdot$$

Dissociation of the hydrogen bromide may be effected by peroxide decomposition or by photolysis with ultraviolet light. Termination steps have not been detected experimentally but are probably radical-radical combinations.

While the scope of the reactions has been explored quite extensively,[4] the mechanistic details were overlooked until about a decade ago. The findings of Goering, Abell and Aycock,[5] demonstrating a stereospecificity in the addition of hydrogen bromide to 1-bromocyclohexene and 1-methylcyclohexene (yielding *cis*-1,2-dibromocyclohexane and *cis*-1-methyl-2-bromocyclohexane respectively) spurred the investigation of the stereochemistry of the reaction and reopened the question of mechanism. The proposals of Kharasch and Hey give no expectation of stereospecificity and, in general, addition reactions of free radicals to olefins are expected to proceed by way of planar radical intermediates, with products determined largely by thermodynamic control. A substantial number of hydrogen bromide additions now have been shown to proceed stereospecifically by a *trans* addition of the elements of hydrogen and bromine and to be independent of thermodynamic stability in the isomer produced. These include both cyclic and non-cyclic olefins and acetylenes. In general, stereospecificity seems to be favored by low temperatures and high hydrogen bromide concentrations.

Several rationalizations have been offered to account for the preference for the *trans* addition mechanism. Goering, Abell and Aycock[5] suggested a bridged, or at least a resonating bromine atom, holding both carbons of the double bond in fixed conformation until hydrogen abstraction completes the structure from the side opposite the bromine bridge. A second possibility is that the hydrogen abstraction step follows so closely on the heels of the bromine atom addition to the pi bond that changes in conformation of the initially formed bromoalkyl radical do not have a chance to take place.[6] A third suggested possibility[6,7] is that the olefin complexes with the hydrogen bromide, and that collision with a bromine atom gives a simultaneous attachment of this attacking bromine and a breaking of the hydrogen–bromine bond of the complexed hydrogen bromide, bonding the hydrogen and freeing a new bromine atom to continue the chain. Unfortunately, evidence for or against any one of the three possibilities is scanty. The recent paper by Skell, Allen and Gilmour,[8] demonstrating a high mobility of the bromine atom when it is attached to a carbon adjacent to a free radical site, lends possible support to the bridging hypothesis. In that investigation abstraction of a primary hydrogen from isopropyl bromide or *t*-butyl bromide produced migration of the bromine to the terminal carbon. On the other hand, the hydrogen abstraction step has been demonstrated by Skell and Allen[9] to be quite rapid, at least relative to hydrogen abstraction by the thiol radical. In their study of methyl mercaptan addition of olefins, the reaction becomes quite stereospecific in the presence of hydrogen bromide, indicating that the latter is a better chain transfer reagent than methyl mercaptan. The hydrogen bromide–olefin complex hypothesis has not yet been shown to be significant in free radical reactions.

It is unfortunate that kinetic data are quite limited on the hydrogen bromide-olefin reaction, since this would be of great help in defining a mechanism. The only data available are the investigation of Armstrong and Spinks[10] on the gas phase reaction of ethylene with hydrogen bromide. They observed a first order dependence of the rate on ethylene concentration at high ratios of hydrogen bromide to ethylene, and a slightly greater than second order dependence on hydrogen bromide concentration. Their estimate of chain length is of

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[1] This research was supported in part from a grant from the Research Corporation and in part from a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of those funds.

[2] M. S. Kharasch, H. Englemann and F. R. Mayo, *J. Org. Chem.*, **2**, 288 (1937).

[3] D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

[4] F. R. Mayo and C. Walling, *ibid.*, **27**, 351 (1940).

[5] H. L. Goering, P. I. Abell and B. F. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952).

[6] H. L. Goering and D. W. Larsen, *ibid.*, **81**, 5937 (1959).

[7] H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

[8] P. S. Skell, R. G. Allen and N. D. Gilmour, *ibid.*, **83**, 504 (1961).

[9] P. S. Skell and R. G. Allen, *ibid.*, **82**, 1511 (1960).

[10] D. A. Armstrong and J. W. T. Spinks, *Can. J. Chem.*, **37**, 1210 (1959).

the order of 10^5, and they assign the bromine atom reaction with ethylene as the rate determining step. Their data are somewhat suspect, however, since they initiate the reaction with gamma rays from a cobalt-60 source which are easily capable of dissociating bonds other than the hydrogen–bromine bond. Also, of course, their data are obtained for the gas phase, whereas all of the data on stereochemistry have been obtained from liquid phase reactions.

It was with this background in mind that attention was turned to the use of electron paramagnetic resonance (EPR) spectroscopy as a very powerful tool for examining the structure of the intermediate bromoalkyl radical. It was hoped that the EPR technique would yield information not only as to the structure of the radical intermediate, but also confirm the correct sequence of addition of the hydrogen and bromine atoms.

Mitchell, Greene and Spinks[11] have used EPR to examine the reaction of hydrogen bromide with ethylene, again using gamma rays as their initiating agent, but without observing any structure ascribable to the bromoethyl radical. Nevertheless it seemed likely that judicious choice of olefins and reaction conditions might enable one to observe these intermediate radicals, and, of course, a well-defined spectrum can give detailed information on the structure of the radicals. It is quite obvious that observation of a radical with specific structure does not necessarily implicate that structure as the intermediate controlling the stereochemistry of the reaction, although it can certainly lend support to one of the three hypotheses.

Experimental

Olefins.—Cyclopentene and vinylcyclohexane were obtained from Aldrich Chemical Company. They were purified by fractional distillation through a highly efficient column, and only material homogeneous to gas chromatography was used.

The cyclohexene was obtained from Distillation Products Industries, fractionally distilled and checked for purity by gas chromatography.

The 2-butyne and 3-hexyne were obtained from Columbia Organic Chemicals and found to be pure without further treatment.

cis- and *trans*-2-Butene, ethylene and propylene were purchased in cylinders from the Matheson Company. They were used without purification.

3-Hexene was prepared by the Raney nickel hydrogenation of 3-hexyne by the method of Campbell and Eby.[12] The product was the pure *cis* isomer.

Hydrogen Bromide and Deuterium Bromide.—Anhydrous hydrogen bromide was used as supplied by the Matheson Company in cylinders. The anhydrous deuterium bromide was supplied by Volk Radiochemical Company in 99.8% purity.

Ultraviolet Light.—A GE H85C3 medium pressure quartz mercury lamp was used in conjunction with a Corning 1.69 CS filter.[13] The latter cuts off at about 280 mμ and has a maximum transmission at 390 mμ with about 75% transmission at 360 mμ. Temperature variation and control were the same as described elsewhere.[13]

Sample Preparation.—All samples were prepared on a vacuum line and were thoroughly degassed. Olefins were distilled from sodium metal into the quartz sample tubes under vacuum. After degassing, the hydrogen or deuterium bromide was condensed and frozen a few mm. above the olefin sample. Usually one-fourth to one-half the total sample volume was hydrogen bromide, but since, as noted below, mixing was always incomplete, the relative volumes were not of great consequence. The tube was sealed off under vacuum and the contents mixed by partial warming just before insertion into the liquid nitrogen filled dewar in the spectrometer. The mixing was only partial since experience showed that the most intense signals were observed with a minimum of warming and consequently the least departure from the glassy state. All samples were checked for paramagnetic resonance signals before irradiation by the ultraviolet light.

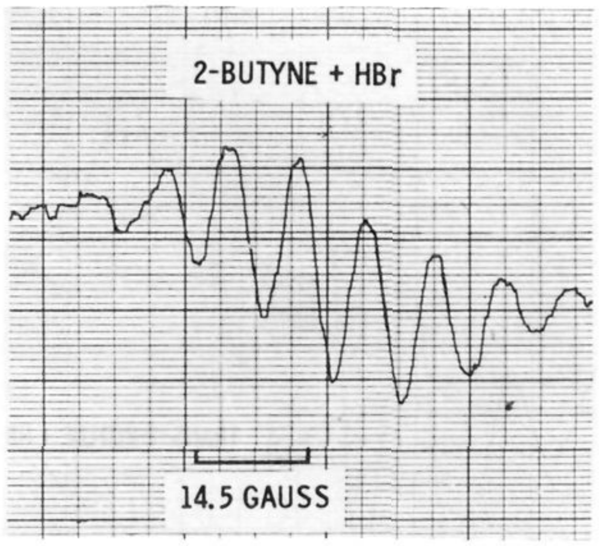


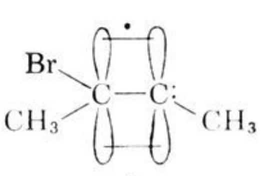
Fig. 1.—Free radical obtained from a mixture of 2-butyne and HBr. Photolysis about 10 min. at 77°K.

Results

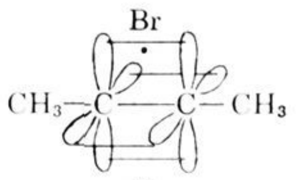
2-Butyne + HBr.—The first derivative of the electron paramagnetic resonance (e.p.r.) spectrum obtained by addition of hydrogen bromide to 2-butyne and photolyzing the system at 77°K. is illustrated in Fig. 1. The free radical was formed in less than four minutes after the light was activated, and steadily increased in concentration, remaining stable even after the light was extinguished. No radical was obtained upon irradiation of the 2-bromo-2-butene product. In all of the olefins studied, no free radical was formed in the parent compound nor in the bromoalkyl product when subjected to ultraviolet irradiation at 77°K.

The spectrum consists of seven equally spaced lines with a hyperfine constant of 8.3 gauss. The multiplet is attributed to a splitting of the unpaired electron by the six equivalent methyl hydrogens. Such a pattern is consistent with a structure in which the unpaired electron spin density is the same at the two terminal methyl groups.

Two possible structures for the radical are



I



II

In structure (I), upon addition of the Br atom, two electrons will probably go into the available sp^2 orbital on the carbon since it is more stable than the pi orbital. The unpaired electron will go into the bonding pi orbital, where it can couple to the six methyl hydrogens by means of a hyperconjugative interaction. This type of interaction involves a spatial overlap between the 1s orbitals of the hy-

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[11] F. W. Mitchell, B. C. Greene and J. W. T. Spinks, *Can. J. Chem.*, **38**, 689 (1960).

[12] K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **63**, 216 (1941).

[13] L. H. Piette and W. C. Landgraf, *J. Chem. Phys.*, **32**, 1107 (1960).

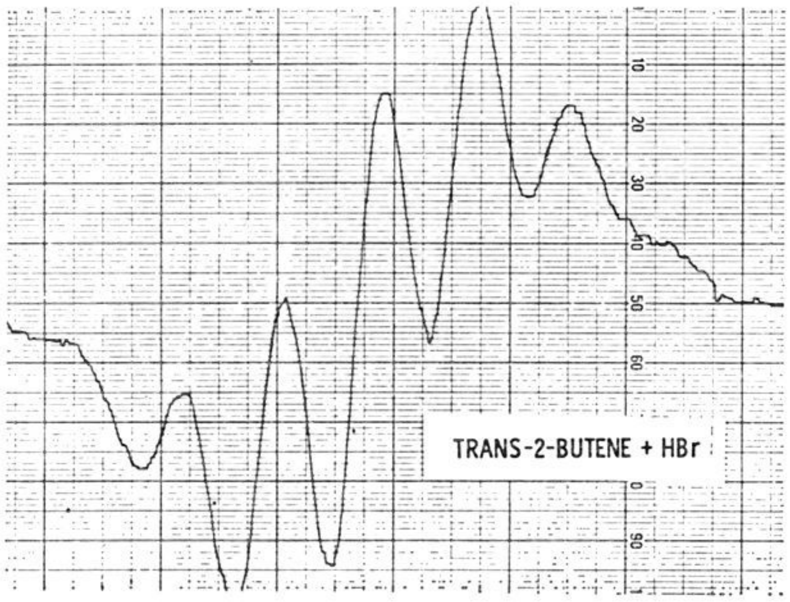


Fig. 2.—Free radical obtained from a mixture of *trans*-2-butene and HBr. Photolysis about 7 min. at 77°K.

drogens and the $2p_z$ orbitals of the pi electron system. Such an interaction is similar to that of the methyl hydrogens with the pi electron system of the ring in the tetramethylsemiquinone negative ion.[14] The magnitude of the interaction will be the same at all six hydrogens provided the Br does not exert a distortion upon the hydrogen wave function of the CH_3 adjacent to it. If the interaction is not the same, one would expect a hyperfine pattern of a quartet of quartets. In structure (II) the Br atom is assumed to bridge the two carbons perpendicular to the plane of the molecule and again put the unpaired electron in the pi system where it can interact with the six hydrogens. The bridged structure now allows an equal interaction and would yield a symmetrical seven line pattern.

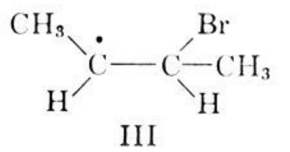
3-Hexyne + HBr.—The spectrum obtained from the 3-hexyne–HBr mixture during photolysis was observed to form at a much slower rate than with the 2-butyne and was not completely resolved. The lack of resolution in radicals formed in glasses such as these is probably due to incomplete averaging of the anisotropic hyperfine interaction. The spectrum, however, was discernible as a major five line spectrum with additional splittings that were not resolved. The five line splitting was measured to be about 19 gauss, and the other splittings appear to be separated by 4 gauss.

The spectrum is a result of the unpaired electron coupling strongly to the four equivalent beta methylene hydrogens and more weakly to the six gamma methyl hydrogens. The spectrum can be explained by two structures similar to those for 2-butyne, except one would expect a stronger hyperconjugative interaction with the methylene than the methyls. It would further be expected that a structure analogous to (I) for 3-hexyne would result in a non-equivalence of the two methylenes because of the proximity of the bromine and therefore not give a major five line pattern.

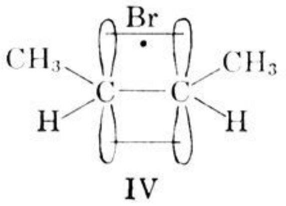
cis- and *trans*-2-**Butene.**—Figure 2 shows the spectrum obtained from *trans*-2-butene with hydrogen bromide. The spectrum of the *cis* isomer was nearly identical. It was observed that the *cis* isomer took longer to form a signal than the *trans* and that its spectrum was not quite as well resolved. The signal from *trans*-2-butene was observed in the steady state at temperatures as high as −175°. At these temperatures the signal disappeared in about 30 sec. The signal was unstable at temperatures as low as −187° but quite stable at −196°.

The spectra for both isomers show identical seven line patterns, but the splittings for the *trans* compound are 12.6 gauss and those in the *cis*, 10.8 gauss. The spectra are interpreted as arising from a splitting of the unpaired electron by the six equivalent methyl hydrogens. Any coupling by the two CH hydrogens is probably less than the line width and is not observed.

Possible structures for the radical intermediates are



III



IV

Structure (III) is similar to the aliphatic radicals generated by Smaller and Matheson[15] and by Cochran and Bowers[16] in which the alpha and beta hydrogens are strongly hyperconjugated to the unpaired electron and are equivalent. Such aliphatic radicals yield typical hyperfine constants of 20–35 gauss. If structure (III) were correct, one would expect six equally spaced lines with a splitting of about 25 gauss.

Structure (IV) assumes that bridging by the bromine atom retains the planarity of the C=C bond and thus allows the unpaired electron to go into the pi orbital and interact by means of hyperconjugation with the two methyls as in the alkyne case. Hyperconjugation is not possible with the single hydrogens on the olefinic carbons. These hydrogens are out of the plane of the pi electron system, and one must therefore invoke a configurational interaction similar to that used in aromatic ions in order for the unpaired electron to have some *s* character at these hydrogens. Such interactions are generally very weak and result in splittings of only a few gauss and could easily be lost in the line width. It is not apparent why there is a difference in coupling constants between *cis* and *trans* isomers, but it certainly emphasizes that they do not give identical radicals.

cis-**3-Hexene + HBr.**—The spectrum of the photolyzed *cis*-3-hexene–HBr mixture gave a poorly resolved five line spectrum with a hyperfine constant of 8.0 gauss. Again, the magnitude of the coupling constant is consistent with a bridged structure similar to the 2-butenes. A non-planar aliphatic radical of the type of structure (III) would also yield a five line spectrum, but the magnitude of coupling would be expected to be about 25 gauss instead of the 8 gauss observed.

Vinylcyclohexane + HBr.—A four line spectrum is observed for vinylcyclohexane with a splitting

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[14] B. Venkataraman and G. K. Fraenkel, *J. Am. Chem. Soc.*, **77**, 2707 (1955).

[15] B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958).

[16] E. L. Cochran and V. A. Bowers, Abstracts of Papers of 134th American Chemical Society National Meeting, Chicago, Illinois, 1958, p. 303.

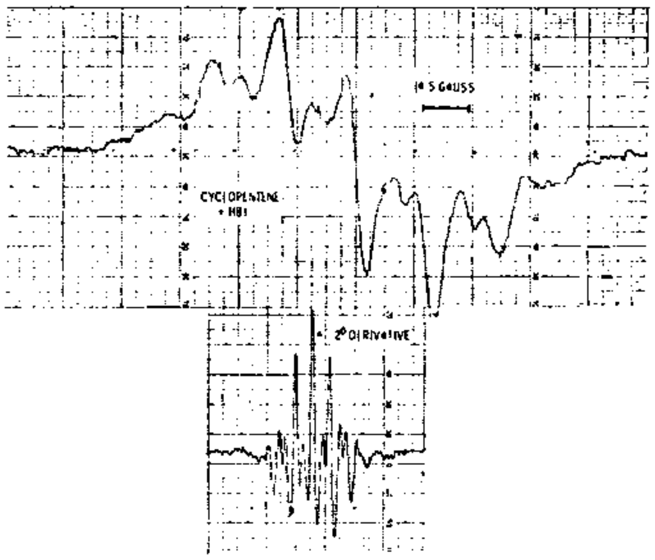
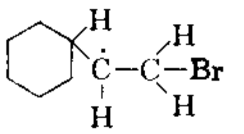


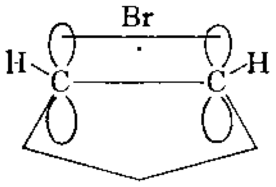
Fig. 3.—(a) Free radical obtained from a mixture of cyclopentene and HBr. Photolysis about 10 min. at 77°K. (b) Second derivative of spectrum in Fig. 3a.

between lines of 16 gauss. The four line spectrum is consistent with a splitting by three equivalent hydrogens. Since none of the hydrogens on the side chain would be expected to interact strongly with the unpaired electron in a bridged structure, there is only the ring hydrogen to couple, which would yield only a doublet. A more conventional radical structure (V) may be a better explanation for the spectrum, in which three hydrogens couple to yield a quartet. Certainly a definite assignment of coupling hydrogens must await further work.



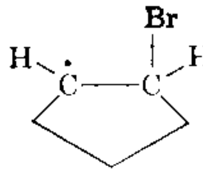
V

Cyclopentene + HBr.—Cyclopentene yields a basic five line spectrum with a splitting of 18.8 gauss, each line of which is split further into a triplet with a splitting of 9.4 gauss. The fact that the smaller splitting is one-half the larger results in some overlap of the lines and a total of eleven lines is obtained (Fig. 3). The eleven lines were more easily discernible, as were the intensities of the lines, in the second derivative displayed in Fig. 3b. The spectrum again seems consistent with the bridged structure (VI) in which a strong hyperconjugation would be expected with the four beta methylene hydrogens, since the ring is rigid, and the hydrogens are not in the plane of the ring. The planarity of the whole ring might account for the strong configurational interaction of the two alpha hydrogens with the unpaired electron, if these are, indeed, responsible for the secondary splitting.



VI

The unbridged structure (VII) also could be expected to give a five line spectrum due to splitting by the possible equivalent alpha and beta hydrogens, but these would be split further into quintets by the gamma hydrogens if any fine structure were to be observed at all.



VII

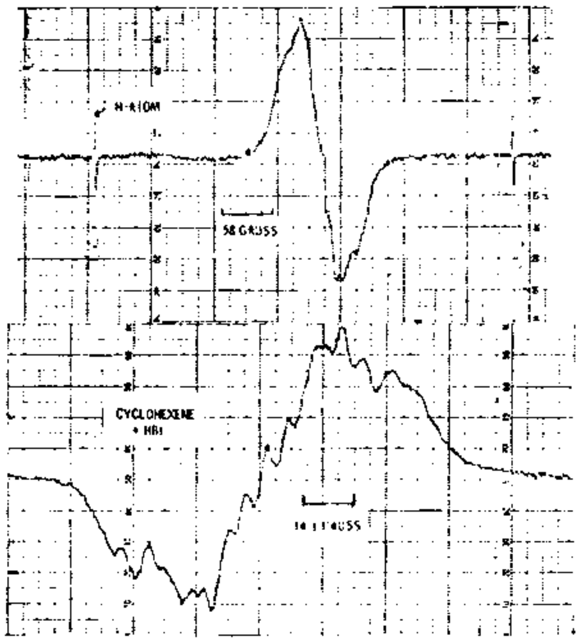
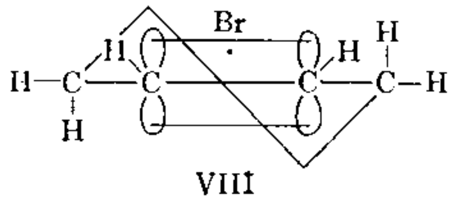


Fig. 4.—(a) Free radical obtained from a mixture of cyclohexene and excess HBr. Photolysis 10 min. at 77°K. Satellite lines are due to H-atoms. (b) Center radical of Fig. 4a expanded.

Cyclohexene + HBr.—Figure 4 shows the radical obtained from cyclohexene. In addition the H atoms that are produced by the decomposition of the HBr also were observed. The H-atom lines were ~500 gauss apart and flank the bromoalkyl radical. These H-atom lines also were observed in the ultraviolet light irradiated solution of hydrogen bromide in pentane. In the present experiment the hydrogen bromide was in excess in the cyclohexene. It will be noticed that the concentration of H-atoms is much less than the bromoalkyl radical, giving support to the chain propagating step as hydrogen abstraction from molecular hydrogen bromide by a bromoalkyl radical. It also should be noted in the same figure that the bromocyclohexyl radical signal does not center at $g = 2.0023$ but is displaced by approximately 20 gauss toward higher field strengths. Such a displacement may be expected when an electron shows spin-orbit coupling with a nucleus such as bromine.

An expanded spectrum under higher resolution for the bromocyclohexyl radical showed a basic three line spectrum with a splitting of 26 gauss, each line of which appears to be split further into at least five lines, with a splitting of 4 gauss. The bridged structure is compatible with a large triplet splitting by the two pseudo-axial beta hydrogens, (VIII), and a second splitting by the pseudo-



VIII

equatorial beta hydrogens, with further splittings by either alpha or gamma hydrogens. The corresponding non-bridged structure would give a basic five line pattern instead of three.

Propylene and Ethylene + HBr.—The spectra obtained for the ultraviolet irradiated ethylene and propylene plus hydrogen bromide, dissolved in pentane were observed to develop very rapidly. Measurable signals were obtained in less than one minute. The spectra appear to be characteristic of a single line anisotropically broadened. Attempts were made to operate at higher temperatures in hopes of improving resolution, but the radicals were too unstable. No interpretation of the spectra is offered.

Experiments with DBr.—Spectra were obtained for 2-butene and cyclopentene plus deuterium bromide, photolyzed at 77°K. These spectra were identical with the spectra obtained with hydrogen bromide. Consequently the same bromoalkyl radical intermediate is formed with both HBr and DBr indicating the Br adds first. It was observed that in every case when deuterium bromide was the source of the bromine atom that the growth of the signal was much slower than with HBr. There may well be some connection here between the isotope effect observed by Goering and Larsen[6] and the slower radical formation observed here.

Although one cannot arrive at an unequivocable conclusion that these electron paramagnetic resonance results definitely establish a bridged intermediate in the hydrogen bromide addition to olefins, it is certainly true that the consistency of the bridged structure in fitting the observed spectra suggest the probability of such a mechanism. It must be pointed out, however, that the bridged structure does not imply a fixed or static structure, but the bridge can be looked upon as resulting from a resonating structure in which the Br atom oscillates between carbons at a frequency greater than or equal to the magnitude of the hyperfine interaction = 5.0×10^7 c.p.s. Such an oscillating scheme would yield the same symmetrical spectra observed. In addition, the following points now have been well established; that the bromine atom addition is the initial event in the sequence of addition and that the extreme rapidity of the reaction in the solid, glassy phase has been demonstrated. It is equally obvious that much work yet remains to be done, including extensive studies with deuterium substituted olefins. Such experiments are being planned.

Acknowledgments.—Thanks are due Miss Kathleen Doyle for her assistance in preparation and gas chromatography of a number of the olefins, and to Prof. P. S. Skell for his discussions and suggestion of the oscillating Br atom type structure.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE PLASTICS COMPANY, DIVISION OF UNION CARBIDE CORPORATION, BOUND BROOK, NEW JERSEY]

Transition Metal Catalysts. IX. Random Ethylene–Propylene Copolymers with a Low Pressure Polymerization Catalyst

BY GEORGE W. PHILLIPS AND WAYNE L. CARRICK

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Ethylene–propylene copolymers were prepared at atmospheric pressure with the VCl_4-$(C_6H_5)_4Sn$-$AlBr_3$, hydrocarbon-soluble, polymerization catalyst. A controlled rate of initiation and thus a constant comonomer composition were obtained by the introduction of a constant amount of oxygen into the monomer stream. Three copolymers, containing 2.6, 3.8 and 10 mole % propylene, were found to have uniform comonomer compositions when fractionated by successive extraction with boiling solvents, in contrast to copolymers prepared with other reported Ziegler-type catalysts. An elution fractionation of the 10 mole % propylene copolymer was conducted with cellosolve–xylene mixtures above the copolymer melting point. The molecular weight distribution was shown to approximate the "most probable" distribution. This is in agreement with a previously proposed polymerization mechanism. The propylene contents of each of the fractions from the 10% copolymer were within ±1% propylene of the value of the whole copolymer. This narrow composition distribution is in accord with the statistical distribution predicted theoretically for random copolymers and is in accord with the previous finding that $r_1 \cdot r_2 \cong 1$. These data suggest that Ziegler-type catalysts containing a single active species are amenable to the same statistical and kinetic treatment that has been used for the classical polymerization catalysts.

Introduction

In the copolymerization of two vinyl monomers, there are four separate propagation reactions[1]

$$\begin{aligned} M_1^* + M_1 &\xrightarrow{k_{11}} M_1^* \\ M_1^* + M_2 &\xrightarrow{k_{12}} M_2^* \qquad (1) \\ M_2^* + M_2 &\xrightarrow{k_{22}} M_2^* \\ M_2^* + M_1 &\xrightarrow{k_{21}} M_1^* \end{aligned}$$

where M_1 and M_2 are the two monomers and M_1^* and M_2^* are the growing polymer chain ends terminated by M_1 and M_2, respectively. The reactivity ratio, r_1, is defined as k_{11}/k_{12} and r_2 as k_{22}/k_{21}. When $r_1 \cdot r_2 = 1$, the above equations predict that the resulting copolymer should contain a random distribution of the two monomer units along the polymer chains. Stockmayer[2] has given an extensive statistical treatment of copolymer composition distributions and has concluded that when $r_1 \cdot r_2 \sim 1$ and the degree of polymerization is high, compositional variations between polymer molecules should be quite small with the result that the gross copolymer would be very homogeneous.

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(1) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953, Chapter V.

(2) (a) W. H. Stockmayer, *J. Chem. Phys.*, **13**, 199 (1945). (b) R. Simha and H. Branson, *ibid.*, **12**, 253 (1944).