Table III. Strain Energies in Aromatic Hydrocarbons

	$\Delta H_f°$(s), kcal./mole	Strain energy, solid, kcal./mole	ΔH, sublimation, kcal./mole	$\Delta H_f°$(vap), kcal./mole	Strain energy, vapor, kcal./mole
I 2,7-Dimethylphenanthrene	8.7 ± 0.6[a]	12.6 ± 1.5	25.5 ± 0.2	34.2 ± 0.6	12.1 ± 1.5
II 4,5-Dimethylphenanthrene	21.3 ± 1.4[a]		25.0 ± 0.3	46.3 ± 1.4	
III 2,4,5,7-Tetramethylphenanthrene	3.8 ± 0.8	2.6 ± 1.1	27.3 ± 0.4	31.1 ± 0.9	7.2 ± 1.4
IV 3,4,5,6-Tetramethylphenanthrene	6.4 ± 0.7		31.9 ± 0.9	38.3 ± 1.1	
V Phenanthrene	27.5 ± 0.6[b,c]		20.7 ± 0.5[d]	48.2 ± 0.8	
VI 3′,6-Dimethyl-1,2-benzanthracene	18.2 ± 0.7[a]	15.0 ± 0.7	26.9 ± 0.4	45.1 ± 0.8	15.0 ± 1.1
VII 1′,9-Dimethyl-1,2-benzanthracene	33.2 ± 0.7[a]		26.9 ± 0.8	60.1 ± 1.1	
VIII 1,2-Benzanthracene	40.6 ± 0.6[c]		25.0 ± 0.5[e]	65.6 ± 0.8	

[a] Reference 2. [b] H. Skinner, private communication. [c] A. Magnus, H. Hartmann, and F. Becker, *Z. physik. Chem.* (Leipzig), **197**, 75 (1951). [d] R. S. Bradley and T. G. Cleasby, *J. Chem. Soc.*, 1690 (1953). [e] J. D. Kelley and F. O. Rice, *J. Phys. Chem.*, **68**, 3794 (1964).

for V, the same material as used for the combustion experiments. These are shown in Table III together with data for the parent compounds.

The differences between the heats of formation of I and phenanthrene (V) are 18.8 kcal./mole in the solid and 14.0 kcal./mole in the vapor and are similar to the corresponding differences between II and III, 17.5 and 15.2 kcal./mole, respectively. This indicates that the addition of the 2,7-dimethyl groups does not appreciably affect the stability of the molecule, even though the increment in the vapor phase is slightly smaller than the usual 15.7 kcal./mole.

In the vapor, from the data on I and II, one derives a strain energy of 12.1 ± 1.5 kcal./mole for the 4,5-methyl group interaction. This must be considered as a lower limit, since phenanthrene itself is nonplanar owing to interference between the 4,5-hydrogens, but the magnitude of this effect is not known. By comparison, the data for compounds III and IV, which contain the same 4,5-methyl group interaction, but with CH_3 buttressing groups in the 3,6-positions instead of H atoms, show a difference in the stabilities of 7.2 ± 1.4 kcal./mole. These CH_3 groups are causing 7.2 kcal./mole more distortion than do H atoms in the 3,6-positions and thus exerting a buttressing effect, making compound IV less stable. Since ΔH_f[3,6-dimethylphenanthrene(s)] ≈ 11.9 ± 1.0 kcal./mole, one would have predicted ΔH_f[3,4,5,6-tetramethylphenanthrene(s)] ≈ −6 kcal./mole based on the 18-kcal./mole increment established from the I–V and II–III data, but this becomes ∼+6 kcal./mole when allowance is made for the 4,5-strain energy.

The differences in the heats of formation of 1,2-benzanthracene and 3′,6-dimethyl-1,2-benzanthracene are 22.4 and 20.5 kcal./mole in the solid and vapor phases, respectively, which are larger than those in the phenanthrenes. The lattice energies of 3′,6- and 1′,9-dimethyl-1,2-benzanthracenes are identical, and the difference in their heats of formation is 15.0 kcal./mole. This is larger by 3.0 kcal./mole than that between the dimethylphenanthrenes, and the deviation is of the same sign as the change observed on substituting 3,6-methyl groups for 3,6-H atoms on the phenanthrenes. One concludes that the fused ring sterically approximates a methyl group located at the same position.[18]

Acknowledgments. This work has been supported financially by the National Science Foundation, by the Petroleum Research Fund of the American Chemical Society, and by the Robert A. Welch Foundation.

(18) M. S. Newman and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1537 (1941).

Gaseous Products from Interactions of Recoil Carbon-11 Atoms with Liquid Hydrocarbons[1a]

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Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa. *Received July 21, 1965*

The chemical behavior of recoil carbon-11 in different types of C_5–C_7 hydrocarbons has been investigated by determining the radiochemical yields of gaseous products containing ^{11}C, in order to clarify the mechanism for the formation of these products. Initial studies showed that iodine scavenger lowers the yields of all of these products except acetylene, while increased radiation dose increases the yields of products other than acetylene. Individual and relative yields of the two-carbon products are shown to be highly dependent on the structure of the target molecules. The results are discussed in terms of the decomposition modes available to the activated complexes assumed to result from insertion-type reactions of three primary species: ^{11}C, ^{11}CH, and $^{11}CH_2$. Reactions of recoil ^{11}C atoms with mixtures of benzene and methylcyclopentane were studied. The yields of these products are approximately linear functions of the molar concentrations of the two components.

(1) (a) Work was performed at the Ames Laboratory of the U. S. Atomic Energy Commission, Contribution No. 1748; (b) work done in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

Introduction

The chemical behavior of recoil carbon atoms has aroused considerable interest in recent years. Although most of the papers published on this subject have dealt with reactions in the vapor phase, some studies of condensed systems have been reported. It has been shown that the yields of the major ^{11}C-labeled products vary with phase.[2–6] Thus, in order to completely characterize the behavior of energetic carbon atoms toward a given compound, it is necessary to have information concerning the distribution of products from different phases. In this paper, the yields of methane-, ethane-, ethylene-, and acetylene-^{11}C obtained from various liquid hydrocarbon targets are presented.

Preliminary studies on the effects of radiation dose and of iodine scavenger on the gaseous products from ^{11}C plus liquid cyclohexane have been reported.[7] More recent results for other systems make possible somewhat different conclusions concerning the influences of these parameters.

Our present data indicate that the yields of C_2 products are related to the structure of the target compounds. Although similar trends have been reported for the products from O_2-scavenged gaseous targets[8,9] and I_2-scavenged liquid targets,[10] the trend observed here is for pure hydrocarbons irradiated in the liquid phase.

Experimental Section

Research grade hydrocarbons obtained from Phillips Petroleum Co. were used. Their stated purities were usually in excess of 99.95 mole %. Samples containing 0.15–0.30 g. of hydrocarbon were sealed in Pyrex glass bulblets after being degassed on a vacuum line. Irradiations were made with the bremsstrahlung beam of an electron synchrotron at Iowa State University, which produced ^{11}C *in situ* by the $^{12}C(\gamma,n)^{11}C$ reaction. Electron energies of 47 or 70 Mev. were used in the runs; the results at the two energies were identical. The frequency of the electron pulses was 60 c.p.s. and the duration of each pulse was about 4×10^{-8} sec.

The $^{12}C(\gamma,n)^{11}C$ reaction used in this study is endoergic to the extent of 18.7 Mev. The excess γ-ray energy in each case must be shared by the emitted neutron and the carbon-11 atom. Since the cross section for this reaction is largest for γ rays with energies of 20–25 Mev., typical recoil energies are on the order of 0.5 Mev.[11]

Although the recoil atoms are initially formed at very high energies, it is assumed that they will not undergo chemical reactions until most of their energy is dissipated. For this reason, the results should apply in general to carbon atoms that are excited to energies of the order of 10–30 e.v. and allowed to react with these systems.

It has been shown that the initial charges on the carbon-11 atoms are +1 or +2.[12,13] However, it has also been demonstrated that such charges will have been lost in collisions well before the atom or radical has reached the energy region for stable recombination.[5,13] The maximum range that might be expected for the recoil atoms in these liquid hydrocarbons is $\sim 10^{-3}$ cm.; this distance will be traversed in $\sim 10^{-9}$ sec.[13] Because the time between beam bursts is much longer, $\sim 10^{-2}$ sec., all of the carbon-11 atoms formed in one burst will have reacted before the next one occurs.

In some of the early experiments, a tantalum foil was wrapped around each bulblet to serve as a monitor of the γ-ray flux. For each run the tantalum-180m activity produced by the $^{181}Ta(\gamma,n)^{180m}Ta$ reaction was taken to represent the relative number of ^{11}C atoms produced, after corrections were made for the different rates at which the two decayed.[7,10] In most of the experiments reported here, the samples themselves were used as γ-ray monitors by counting them in their bulblets in a standard geometry above a 2.5 × 2.5 cm. NaI(Tl) crystal prior to their introduction into the gas chromatograph. Some activation occurred in the glass of the bulblets, giving mostly short-lived nuclides, such as 2.0-min. ^{15}O. Since the samples were not counted until 12 min. after the irradiations, nearly all of the observed counts were due to the 20.4-min. ^{11}C.

Separation of the products was accomplished by gas–solid chromatography, using silica gel (14–20 mesh) as the solid material. A gas chromatograph, designed and built by R. Clark and W. Stensland of this laboratory, was used in the isothermal mode at operating temperatures of 20–60°. Glass columns were used which varied in length from 1 to 4 m. and had internal diameters of 0.6 cm. They were flushed with helium for several hours prior to each run. Carrier compounds were commonly added to ensure that some of the tracer amounts of material were not being lost. This was particularly important for acetylene because of its high reactivity. Results obtained with and without the addition of carriers were the same. Flow rates of about 40–50 ml./min. were used in all runs.

Radioassay of the products eluted from the chromatographic columns was done by a flow-counting method previously described.[7,10] Scintillation counting of the annihilation radiation was used to measure the activity of each product. A single-channel analyzer was used to discriminate against pulses corresponding to γ-ray energies below 0.4 Mev.

In order to determine the absolute radiochemical yields, the total ^{11}C content of several irradiated samples was determined. The bulblets were broken and the samples, vaporized in a stream of helium gas, were swept over a bed of copper oxide at 750°, oxidizing

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(13) D. B. DeVries and A. F. Voigt, U. S. Atomic Energy Report IS-886, Iowa State University of Science and Technology, Ames, Iowa, Institute for Atomic Research, 1964; *Dissertation Abstr.*, **25**, 2777 (1964).

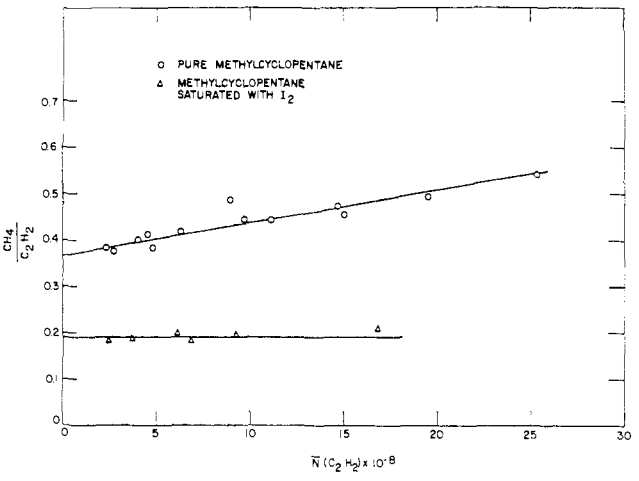

Figure 1. Methane-^{11}C/acetylene-^{11}C ratio *vs.* dose for methylcyclopentane.

them completely to carbon dioxide and water. The gases then passed through a sulfuric acid scrubber, which effectively removed all of the water. For each sample, the carbon dioxide was frozen in a liquid nitrogen trap so that it could be collected without also having to collect an excessive amount of the helium gas. After all the carbon dioxide was trapped, the liquid nitrogen dewar was removed, and the gas was allowed to expand into a collection vessel along with some helium used to purge the trapping vessel. Portions of the resulting gaseous mixture were then transferred to a gas buret in which the volume of each portion was determined; the summation of those measurements gave the total volume of carbon dioxide and helium collected. An aliquot from each portion was passed through the chromatograph and counting cell. The total volume of carbon dioxide was calculated by comparison of the area of the thermal conductivity peak for each aliquot with the area for a standard amount of carbon dioxide.

The amount of carbon dioxide recovered in these measurements agreed with that expected from the original sample weight, indicating quantitative conversion to and recovery of the carbon dioxide. The total amount of ^{11}C as measured in the flow counter was thus related to the unit of monitor response, with ^{180m}Ta the monitor in these experiments.

Following the combustion experiments, samples of methylcyclopentane were irradiated and assayed in the usual way. The acetylene-^{11}C yield was compared with the total ^{11}C yield through the common monitor and was determined to be 17.8% for methylcyclopentane. This number was used as a secondary standard. In the main part of the experiments in which the total activity in the bulblet was used as a monitor, absolute product yields were calculated by comparison with the results for acetylene-^{11}C from irradiated methylcyclopentane.

The radiation dose received by the samples was determined by two methods, the Fricke dosimeter and a cobalt glass dosimeter,[14] which gave similar results of approximately 2×10^{-3} e.v./molecule/min. of an irradiation of average intensity.

(14) N. J. Kreidl and G. E. Blair, *Nucleonics*, 17, No. 10, 58 (1958).

Results

Irradiations of varying duration and dose were made on methylcyclopentane and methylcyclohexane and on methylcyclopentane containing approximately 10^{-3} mole fraction of iodine. The yield of acetylene-^{11}C from methylcyclopentane was unaffected by the presence of iodine scavenger, in agreement with the results for other systems. It was also nearly constant over the dose range investigated, 0.006 to 0.06 e.v./molecule, so that it could be used as an internal monitor as previously described.[7,10,11] As an indicator of dose, the quantity $\bar{N}(C_2H_2)$ was calculated for each run according to eq. 1, where R represents the observed

$$\bar{N}(C_2H_2) = Rft/w(1 - e^{-\lambda t}) \qquad (1)$$

counts due to acetylene at the time when the beam is turned off, f is the flow rate in ml./min., t is the irradiation time in min., w is the sample weight in grams, and λ is the decay constant for ^{11}C. This quantity $\bar{N}(C_2H_2)$ may be considered to be proportional to the number of labeled acetylene molecules formed per gram of sample and therefore proportional to the dose. From the dosimetry measurements the proportionality constant can be estimated as $(2.3 \pm 0.5) \times 10^{-3}$ e.v./molecule per $\bar{N}(C_2H_2) \times 10^{-8}$.

The effects of radiation dose and iodine scavenger on the ratio CH_4/C_2H_2 for methylcyclopentane samples are shown in Figure 1. The dose in e.v./molecule can be estimated by multiplying the abscissa by 2.3×10^{-3}. The ratio appeared to be independent of dose over the range 0.006 to 0.04 e.v./molecule for the iodine-containing samples, in agreement with earlier observations.[7] For pure samples of methylcyclopentane, however, the ratio increased with dose and the value extrapolated to zero dose was larger than that for scavenged samples. This curve of yield *vs.* radiation dose does not agree with those published previously[7] in which the curves for unscavenged systems appeared to be nonlinear, extrapolating at low dose to values equivalent to those obtained for scavenged samples. It now appears that those extrapolations were incorrect, based upon insufficient data at low dose, and that the yields of methane, ethylene, and ethane are different for scavenged and unscavenged systems even at "zero dose."

For the irradiation of methylcyclopentane the effects of varying the parameters of dose and scavenger on the fraction of the C_2 products which appear as ethylene plus ethane are shown in Figure 2. The columns used effectively separated ethylene and ethane; the two yields were added for this curve. The ethane yields were low; approximately 0.8% of the total ^{11}C appeared as ethane. The ethane/ethylene ratio was 0.163 ± 0.007 in twelve experiments without scavenger and 0.184 ± 0.005 in six experiments with added I_2. The fraction of C_2 products appearing as ethane showed some increase as dose was increased, but the uncertainty in the slope of the curve of this fraction *vs.* dose was larger than the slope itself. The average ethane fraction in the experiments without scavenger was 0.038 ± 0.002 and with scavenger 0.028 ± 0.002. Corresponding values for ethylene were 0.234 ± 0.003 and 0.152 ± 0.012. This amounts to 26% reduction in the ethane fraction and

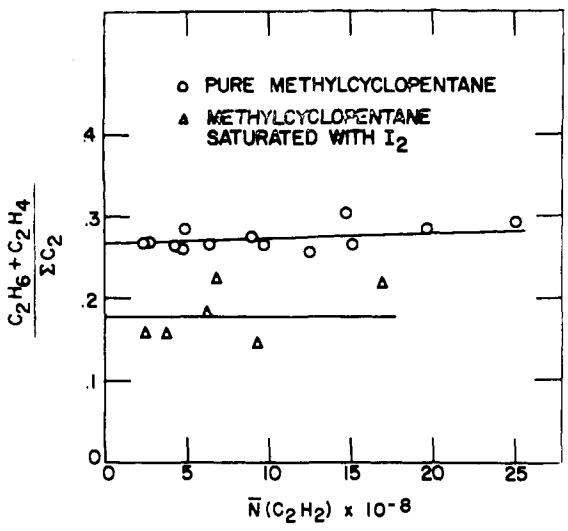

Figure 2. Yield of ethane plus ethylene compared to the total C_2 yield *vs.* dose for methylcyclopentane.

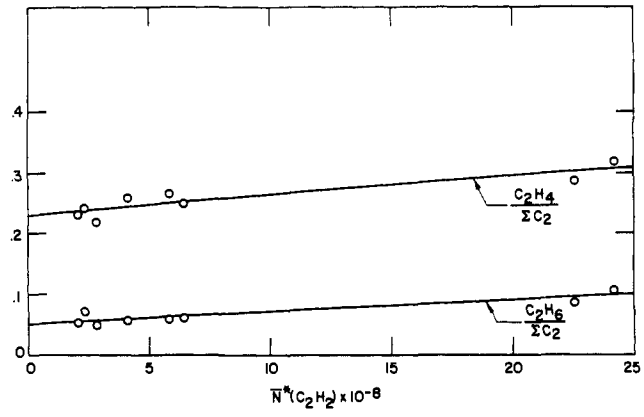

Figure 3. Yields of ethane and ethylene compared to the total C_2 yield *vs.* dose for methylcyclohexane. The quantity $\bar{N}^*(C_2H_2)$ was calculated by multiplying the results obtained from eq. 1 by 17.8/11.6 (Table II) in order to compare the internal dose monitor in this system to that used for methylcyclopentane (Figures 1 and 2).

35% in the ethylene fraction upon the addition of scavenger.

In the case of methylcyclohexane a dose study over the range 0.005 to 0.06 e.v./molecule was made without scavenger. Results are shown in Figure 3 as the fractions of the C_2 products in the form of ethane and ethylene.

Although these results indicate that the yields of some of the recoil products depend upon dose, they also show that extensive dose studies are not necessary in order to characterize a system. For samples irradiated for about 5 min., $\bar{N}(C_2H_2)$ was typically $\sim 5 \times 10^8$, the dose was $\sim$0.01 e.v./molecule, and the yields were not appreciably different from those which would have been obtained by determining them as a function of dose and extrapolating to zero.

Radiochemical yields, defined as the fraction of total ^{11}C observed as a particular product, are given in Table I for the volatile products from various iodine-scavenged systems and in Table II for unscavenged systems. In general the results reported are the average values for three to six runs under low dose conditions, $\sim$0.01 e.v./molecule; the agreement among runs was usually quite good. The target compounds were chosen to include a variety of different structure types: straight- and branched-chain compounds, olefins, cyclics, and aromatics.

Table I. Radiochemical Yields from Iodine-Containing Samples

Hydrocarbon target	Yield, %			
	CH_4	C_2H_6	C_2H_4	C_2H_2
2,2-Dimethylbutane[a]	3.7		14.9[b]	30.5
n-Hexane	5.1	0.9	5.5	19.8
2,3-Dimethylbutane[a]			11.5[b]	24.5
2-Methylpentane	3.7	0.7	7.9	21.6
Methylcyclopentane	3.4	0.6	3.3	17.8
Cyclohexane[c]	3.6		1.6[b]	12.6

[a] Calculated from data in ref. 10. [b] C_2H_6 and C_2H_4 not resolved. [c] Calculated from data in ref. 7.

The product distributions from benzene and methylcyclopentane are quite different (see Table II). Therefore it was thought worthwhile to irradiate mixtures of the two compounds. Although the results were not conclusive, they indicated that within experimental error the product yields were related in a linear fashion to the molar concentrations of the two components.

Table II. Radiochemical Yields from Pure Hydrocarbon Samples

Hydrocarbon target	Yield, %			
	CH_4	C_2H_6	C_2H_4	C_2H_2
2,2-Dimethylbutane	5.2	2.6	17.9	30.5
2,3-Dimethylbutane	6.6	1.9	14.9	24.5
n-Pentane	8.3	1.5	9.9	22.1
3-Methylpentane	7.4	1.9	10.5	21.8
2-Methylpentane	8.0	2.0	11.6	21.6
n-Hexane	7.9	1.5	7.5	19.8
Hexene-1	2.2	0.5	5.0	18.7
Methylcyclopentane	6.6	0.8	5.8	17.8
Hexene-2	7.6	0.9	5.7	14.7
Methylcyclohexane	5.2	0.8	3.7	11.6
Cyclohexene	2.7	0.5	1.7	13.1
Cyclohexane	6.6	1.1	3.1	12.6
Benzene	0.2	0.0	0.0	5.6
Toluene	0.4	0.1	0.6	4.9

Thus in a 50–50 mixture it appeared that 50% of the labeled products resulted from a final reaction with one of the components and 50% with the other.

Discussion

Radiation Dose and Iodine Scavenger Effects. The effect of increased dose is most noticeable in the methane yield. Since the beam current was approximately constant during these irradiations, an increase in dose implies an increase in duration of the irradiation. Several possible processes could lead to the observed increase in methane yield. It is usually considered to be the end product of hydrogen-abstraction reactions starting with the initial carbon atom. An alternate reaction is the insertion of a still energetic $^{11}CH_x$ atom (x = 0 to 2) into a C–H bond to form an activated complex too energetic for survival so that the C–^{11}C bond breaks leaving as a radical $^{11}CH_{x+1}$. These mechanisms were proposed for the reactions of meth-

ylene by Kistiakowsky and co-workers.[15–17] Repetition of these steps to the methyl radical would be followed by hydrogen abstraction to form methane since it is not possible for the methyl radical to undergo insertion. Reaction of these radicals with radiolytically produced hydrogen atoms is certainly another feasible path for the addition of hydrogen.

In comparing yields from scavenged and unscavenged systems, Tables I and II, it can be seen, for example, that the methane yield from iodine-scavenged cyclohexane was 3.6%, 3% lower than the 6.6% observed in the pure compound. Schuler[18] has reported that the $^{11}CH_3I$ yield from iodine-scavenged cyclohexane is also approximately 3%. The indication is that the iodine has reacted with $^{11}CH_3$ radicals which would otherwise have abstracted or picked up free hydrogen to form methane, but other free-radical mechanisms cannot be ruled out.

None of the processes mentioned above should show any increase relative to other reactions of the ^{11}C as dose (and time) are increased. One process which might depend directly on dose would be the rupture of $R-^{11}CH_3$ bonds by radiation. Starting with RH molecules rather large amounts of $R-^{11}CH_3$ molecules are obtained as stable products.[8,11] As the concentration of these builds up, constant irradiation by electrons and γ rays will cause an increasing amount of $R-^{11}C$ rupture leading to an increasing concentration of $^{11}CH_3$ radicals. In the absence of iodine scavenger, these radicals would probably form methane by the abstraction of hydrogen.[19] This increasing yield of methane will be accompanied by a decreasing yield of the products with one carbon more than the reactant. Dose studies in which all of the products were determined have revealed that the yields of higher boiling compounds show little dose dependence,[20] but the changes necessary to account for the observed change in methane would be within the experimental error. Thus, the increase in methane yield probably reflects small and unobservable decreases in the yields of many other products.

A second process which can contribute to the increasing yield of methane with dose is radiolytic decomposition of the original compound. This involves only a small fraction of the molecules originally present, but it may, nevertheless, be significant. Since the concentration of radiolysis products increases with dose, the probability that the labeled fragments will interact with these rather than with the parent molecules increases accordingly. It is interesting to note that the yields of gaseous recoil products from benzene were found to be constant over a wide dose range.[13] This is consistent with either of these processes since benzene and the aromatic products formed from it are relatively resistant to radiolytic decomposition.

The change in the yields of ethylene and ethane with dose, while noticeable in the case of methylcyclohexane, was much less so for methylcyclopentane, a difference which is probably more apparent than real. In some cases a slight decrease in the acetylene yield with increased dose has been seen, essentially balancing the increase in the yield of the other two carbon products, since acetylene usually amounts to 70% of the C_2 yield. This would make it appear likely that the increased yields of ethylene and ethane result from radiation-induced reduction of acetylene. However, the rather large part of the yields of these two compounds which remains at low or "zero" dose must have some other explanation.

In the extensive recent work on the reactions of methylene generated by the photochemical decomposition of ketene and diazomethane, ethane has been observed as a minor product and the mechanism proposed for its formation has been the combination of methyl radicals.[15] Such a mechanism very likely accounts for part of the ethane observed in these experiments, particularly that part which is removed by the addition of iodine (about 25% of the ethane in the case of methylcyclopentane). However, neither the combination of methyl radicals nor the reduction of acetylene and ethylene would appear to account for that part of the ethane which is present at zero dose in the presence of iodine. For this we propose the insertion of the $^{11}CH_2$ radical into the RCH_3 molecule (particularly with R = cyclopentyl or cyclohexyl) followed by rupture of the R–C bond to form $^{11}CH_3CH_2$ radicals. The latter should be able to abstract a hydrogen to form ethane more rapidly than they would interact with an iodine scavenger molecule when the latter is present at a concentration of 10^{-3} mole fraction. The reaction in which a $^{11}CH_2$ radical would insert into a secondary carbon followed by two C–C bond ruptures and pick up of two hydrogens seems considerably less likely, but cannot be eliminated as a possible mechanism.

Ethylene is probably produced to some extent by reduction of acetylene, and the combination of methylene radicals in the presence of a third body to carry off excess energy may contribute. However, the principal mode of formation appears to be bond insertion by the ^{11}CH radical as proposed by Wolf.[8] In an $R-CH_3$ molecule this involves only insertion in the C–H bond, rupture of the R–C bond, and rearrangement of electrons. It appears more likely as a reaction mode than insertions of ^{11}C which would require the pickup of a hydrogen atom or $^{11}CH_2$ which would require that a hydrogen be lost.

Since the yields of acetylene were unaffected by the presence of iodine, that product presumably was formed in the solvent cage. The yields of ethane and ethylene were affected by iodine, however, implying that in part their immediate precursors were radicals which escaped the solvent cage. The fractional decreases in the yields of ethane and ethylene in going from the pure to the scavenged systems are seen to be different for the various compounds studied (Tables I and II). The largest relative decrease for $C_2H_4 + C_2H_6$, 4.2 to 1.6%, was observed with cyclohexane, in which each carbon is bonded to two hydrogen atoms. An insertion into a C–H bond of cyclohexane followed by rupture of two β C–C bonds would give a labeled C_2 fragment with four or less hydrogens. By contrast,

(15) H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957).
(16) J. A. Bell and G. B. Kistiakowsky, *ibid.*, **84**, 3417 (1962).
(17) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.
(18) R. H. Schuler, *J. Phys. Chem.*, **68**, 1618 (1964).
(19) For a discussion of the radiation chemistry of hydrocarbons, including the effects of iodine, see J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964.
(20) F. G. Mesich, Ames Laboratory, unpublished results.

the smallest relative decrease, 20.5 to 14.9%, was observed in 2,2-dimethylbutane, in which the most probable insertions involve carbons bonded to three hydrogens, giving labeled C_2 fragments with five or less hydrogens. In the latter case, with more hydrogen available at the reaction sites, yields of the C_2 products were less sensitive to scavenger than in the former, in which hydrogen pickup by diffusive processes (with which reactions with iodine could compete) would be more important.

Yields from Selected Compounds. Benzene is unique in the series of compounds for which results are given in Table II in that neither ethane nor ethylene was observed as a product. Acetylene production in benzene can be explained as resulting from ^{11}C insertion into the aromatic bonds accompanied by migration of hydrogen and the subsequent decomposition of the reaction complexes. It could also arise from insertions of ^{11}C into C–H bonds. The latter mechanism, as well as ^{11}C insertion into C=C bonds, has been proposed for the formation of acetylene from ethylene targets.[6,21,22] The possibility that ^{11}CH insertion may contribute a major part of the acetylene yield has been effectively ruled out by recent experiments by Wolf and Ache.[23] In the irradiation of 50:50 mixtures of C_6H_6 and C_6D_6 they find that only 8.8% of the labeled acetylene is CHCD. If CH (or CD) insertion were of importance a much larger amount of CHCD would be observed.

The activated complexes formed with benzene must have especially favorable modes of stabilization leading to "buildup" products. Only four products with fewer than eight carbon atoms have been observed—methane, acetylene, benzene and toluene—and they account for only about one-fourth of the total activity.[8,11] Most of the activity is probably in the form of products with more than one phenyl group.

Only small amounts of ethane and ethylene were observed to be produced from toluene (Table II), presumably arising from the methyl group. Toluene is similar to benzene, as expected, in that most of the activity is in the form of higher-boiling compounds. The xylenes and ethylbenzene have been observed as products.[8] Styrene might also be expected, but it has not been reported.

A comparison of the products from cyclohexane and cyclohexene (Table II) shows a marked decrease in methane but a relatively smaller decrease in the C_2 yields when going to the olefinic compound. The smaller methane yield probably results from several causes related to the greater reactivity of the olefin. Cyclohexene and other olefins have been shown to act as their own scavengers in radiation decomposition studies.[19] In this instance the olefins may be reacting with thermal free radicals which would contribute to the formation of methane in the absence of scavenger. Another possibility is that the cyclohexene provides greater opportunity for the recoil atom to react to produce stable molecules larger than methane. Presumably methane is formed only after a sufficient number of encounters have occurred which were unsuccessful in producing such molecules. In either case the methane yield mirrors the over-all reactivity of the target compound toward the recoil species either at thermal or higher energies.

The products observed from recoil carbon reactions with *n*-hexane, hexene-1, and hexene-2 are also given in Table II. Comparison of the product spectra from *n*-hexane and hexene-1 leads to conclusions similar to those in the preceding paragraph. However, the methane yield from hexene-2 was relatively high, nearly the same as from *n*-hexane. With hexene-2 molecules there may be a steric hindrance to the approach of the labeled fragment to the double bond, thus complicating the comparison.

An interesting trend is apparent when the yields of C_2 products from the various target compounds (Table II) are compared. The largest yields were obtained from compounds with branched chain structures, and they appear to increase with the degree of branching. A similar trend was noted earlier,[10] but those observations were essentially of liquid hydrocarbons containing iodine. Wolf[8] showed that the ethylene-^{11}C yields from a number of O_2-scavenged gaseous hydrocarbons were dependent on the relative amounts of primary hydrogens in the target molecules. Stöcklin and Wolf[9] also reported on the structural dependence of acetylene-^{11}C yields from those systems.

The trend observed here is to be expected if the fragmentation products do result from insertion reactions. If an insertion event occurs with a primary C–H bond, the activated complex that would be formed can decompose to give a C_2 fragment by rupturing a single C–C bond. On the other hand, if a secondary C–H bond is involved, such a fragment could only be formed by the rupture of two C–C bonds, necessarily requiring more excitation energy.

In comparing the yields of C_2 products from various compounds, ethylene and ethane have been considered together since the ethane yield is small and not accurately known in many cases.

If, as has been proposed,[8] the major portions of the acetylene and ethylene yields arise from insertions into C–H bonds by the ^{11}C and ^{11}CH fragments, respectively, it seems reasonable to suppose that the yields of ethylene (plus ethane) would be more sensitive to the extent of branching in the target molecules than would the acetylene yields. This follows from the reasonable assumption that the ^{11}CH (and $^{11}CH_2$) radicals have lower kinetic energy than the ^{11}C. If these reacting species are produced in the same relative amounts in all liquid hydrocarbons, the absolute per cent yields of ethylene plus ethane should depend primarily on the structure of the parent molecules. This can be expressed by eq. 2, where x, y, and z

$$\%(C_2H_6 + C_2H_4) = Ax + By + Cz \qquad (2)$$

are the respective fractional amounts of hydrogen in $-CH_3$, $-CH_2$, and $-CH$ groups of the target molecule and A, B, and C are the absolute yield contributions of each group. The value for C may be taken as equal to zero, since neither product was observed from benzene. From the yields from liquid ethane reported by Stöcklin and Wolf,[4] a value of 16.6% can be taken for A. In Table II the results for cyclohexane indicate a value of 4.2% for B.

(21) J. Dubrin, C. MacKay, and R. Wolfgang, *J. Chem. Phys.*, **41**, 3267 (1964).
(22) C. MacKay and R. Wolfgang, *Science*, **148**, 899 (1965).
(23) A. P. Wolf and H. Ache, private communication.

The absolute percentage yields for a number of targets were calculated using these values for the constant terms in eq. 2. The results of those calculations are compared with the experimental values in Table III.

Table III. Comparison of Experimental and Predicted Results for the C_2 Yields from Various Liquid Hydrocarbons

Hydrocarbon target	$\%(C_2H_6 + C_2H_4)$ Calcd.	Exptl.	$(C_2H_6 + C_2H_4)/\Sigma C_2$ Calcd.	Exptl.
2,2-Dimethylbutane	14.8	20.5	0.46	0.40
2,3-Dimethylbutane	14.2	16.8	0.42	0.41
n-Pentane	10.4	11.4	0.37	0.34
3-Methylpentane	11.9	12.4	0.39	0.36
2-Methylpentane	11.9	13.6	0.39	0.39
n-Hexane	9.5	9.0	0.35	0.31
Hexene-1	6.6	5.5	0.27	0.23
Methylcyclopentane	7.0	6.6	0.29	0.27
Hexene-2	9.7	6.6	0.33	0.31
Methylcyclohexane	6.5	4.5	0.28	0.28
Cyclohexene	3.3	2.2	0.20	0.14
Toluene	4.1	0.7	0.12	0.12
Propane	13.4	12.8[a]	0.43	0.41[a]
Isobutane	14.9	14.9[b]	0.44	0.46[b]
Ethylene	4.2	~1.7[c]	0.25	<0.2[c]

[a] See ref. 4. [b] MacKay and R. Wolfgang, *Radiochim. Acta*, **1**, 42 (1962). [c] See ref. 6.

The general agreement appears to be good, indicating that the basic postulates may be valid, at least when applied to the alkanes. The disagreement between the experimental and calculated values for the alkenes and toluene is an indication of the additional reaction modes possible with double bonds or aromatic systems. For 2,3- and particularly for 2,2-dimethylbutane, the experimental values were significantly higher than those predicted. This is not unexpected since the $C-CH_3$ bond strengths are especially low for these two compounds and bond rupture following insertion may be expected to be more likely[24] in these than in straight chain or less branched compounds. While the insertion process itself is exothermic and has little or no activation energy, the subsequent steps, leading to rupture or stabilization, will depend on the strengths of C–C bonds. Thus the probabilities that the activated complexes formed with these molecules will fragment can be expected to be larger than for those with the less branched and cyclic alkanes for which the agreement between experimental and calculated values was excellent.

The yield of ethylene, with which ethane has been included for reasons stated earlier, is much larger when its formation can proceed by ^{11}CH insertions and the rupture of a single C–C bond, as is the case in its formation from primary carbon atoms. From the constants of eq. 2 this process appears to be about four times as likely as the production of ethylene from a secondary carbon in which two C–C bonds must be broken. There are other differences between the reactions in these two cases, and a strict comparison is not necessarily valid since different mechanisms may also be involved in the formation of ethylene from a secondary carbon. Ethylene and ethane are not formed from tertiary carbon or other systems in which more than two C–C bonds would have to be broken.

Another interesting trend can be seen from the results in Table II. As the total yield of C_2 products increases from one system to another, a smaller proportion of it appears as acetylene. A similar trend was reported earlier for systems containing iodine.[10] An attempt to express the trend observed here was successful and useful in predicting the ratio of ethane plus ethylene to the total C_2 yield from different unscavenged systems. The following equation was used.

$$(C_2H_6 + C_2H_4)/\Sigma C_2 = Dx + Ey + Fz \quad (3)$$

The terms x, y, and z are again the fractional amounts of hydrogen in $-CH_3$, $-CH_2$, and $-CH$ groups, respectively, in the target molecules; D, E, and F are the ratios resulting from reactions with compounds containing only one type of carbon–hydrogen group. From the results for benzene F was taken as zero and from the cyclohexane results E was found to be 0.25 (Table II). The results of Stöcklin and Wolf on liquid ethane[4] were used to obtain a value of 0.49 for D.

The experimental and calculated values for this ratio are given in Table III; the agreement was excellent for the results of this study, as well as for those published by other laboratories.

The present treatment indicates that once a C_2 fragment has been produced, the amount of hydrogen available at the site of the insertion will be the principal factor in determining the degree of unsaturation in the resulting C_2 molecule. However, it is assumed that the three reacting species, ^{11}C, ^{11}CH, and $^{11}CH_2$, have different probabilities for producing C_2 fragments from insertions into equivalent bonds.

Benzene–Methylcyclopentane Mixtures. In the case of these mixtures the apparent linear dependence of yields on the molar concentration of the components implies that there is little difference in the over-all reactivity of recoil atoms with benzene and methylcyclopentane molecules.

In the discussion of the products from benzene, it was proposed that the acetylene results directly from reactions of ^{11}C. Only relatively small amounts of ^{11}CH and less $^{11}CH_2$ would be formed in benzene, but much larger amounts would be produced in methylcyclopentane. The latter compound, a saturated C_6 hydrocarbon, would be expected to yield relatively large amounts of saturated C_7 products upon reaction with recoil carbon atoms.[8,11] Except for acetylene the major products from methylcyclopentane are probably formed directly from insertion reactions involving ^{11}CH and $^{11}CH_2$ radicals.

It therefore appears that the reaction cross sections for the same carbon-11 fragment with methylcyclopentane and benzene molecules must be similarly related to the energies. This follows from the reasonable assumption that the reacting species will have energies over a whole range of possible values. Thus it could be concluded that these two molecules have nearly the same energy thresholds for their respective reactions with ^{11}C, ^{11}CH, and $^{11}CH_2$. This conclusion would be in agreement with the proposal by Wolfgang and his co-workers,[5,6,22] that the activation energies for insertion reactions involving these species are nearly zero.

(24) A similar argument has been presented by Spinks, *et al.*, to explain the relatively large amounts of methane produced in the radiolysis of branched chain compounds such as 2,2-dimethylbutane: ref. 19, p. 314.

Conclusions

Our results give additional support to the proposed mechanisms for the formation of recoil products from hydrocarbons. Three primary species, ^{11}C, ^{11}CH, and $^{11}CH_2$, all uncharged, appear to be responsible for the products formed in these systems. The reactions involved seem to be formally analogous to insertion reactions into C–H and C=C bonds initially forming activated complexes. These can become stabilized through energy transfer to the solvent cage, can react further to form "buildup" products, or can undergo decomposition forming labeled molecules or radicals. The simplest mode of decomposition involves rupturing the β C–C bonds to give C_2 fragments. The C_2 products formed from those fragments were studied extensively. Products, such as C_3, etc., formed by more complicated modes of decomposition were not determined since they were present in only relatively small amounts. The yields of C_2 products from various liquid hydrocarbons were shown to be related to the structures of the parent molecules, indicating that C–H bonds are indeed the sites at which the reactions occur. The results are in agreement with earlier proposals that the activation energies for insertion reactions involving these primary species are nearly zero.

Acknowledgments. The authors gratefully acknowledge the continued assistance of the synchrotron staff, particularly Dr. A. Bureau and Mr. J. R. McConnell. Mr. R. Clark and Mr. W. Stensland contributed many helpful suggestions concerning the chromatographic and counting systems.

The Photochemical Reaction of Hydrogen Peroxide with Allyl Alcohol-3,3-d_2

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The reaction of hydroxyl radicals, derived from the photolysis of hydrogen peroxide, with allyl alcohol-3,3-d_2 in the frozen state at 77°K. and in liquid solutions in the range 253–350°K. has been studied. An analytical method based on the gas phase reaction of water with sodium mirrors has been developed. For the reaction with sodium, the isotopic separation factor for protium and deuterium in water was found to be 1.8 in the range of 0–35% deuterium. For all the photochemical experiments, abstraction of deuterium atoms was shown to occur with 8.4 ± 2.5% of the hydroxyl radicals formed; the remainder was considered to add to the olefinic bond. Electron spin resonance spectra of irradiated frozen samples showed that absorption of light by the deuterated allyl alcohol leads to cleavage of the carbon–oxygen bond and that the reaction of hydroxyl radicals with the alcohol is consistent with the interpretation that deuterium atoms are abstracted.

Introduction

Photochemical studies of ultraviolet-irradiated hydrogen peroxide in aqueous solutions of allyl alcohol at 0–50° have shown that the principal mechanism is the addition of hydroxyl radicals to the olefinic bond.[1] Evidence for this has also been obtained by Dixon and Norman[2] in electron spin resonance studies of the reaction of hydroxyl radicals, formed by the reaction of titanous ion with hydrogen peroxide, with aqueous allyl alcohol. Electron spin resonance studies of ultraviolet-irradiated solutions of hydrogen peroxide in allyl alcohol in the glassy state at about 90–120°K. indicate that hydroxyl radicals abstract an α-hydrogen atom from the alcohol.[3–5] Thus the reactions

$$H_2O_2 + h\nu \longrightarrow 2OH$$

$$OH + CH_2CHCH_2(OH) \longrightarrow H_2O + [CH_2{=}CH{-}\dot{C}H(OH) \quad \dot{C}H_2{-}CH{=}CH(OH)]$$

yield α-hydroxyallyl radical.

It seemed somewhat surprising to us that abstraction would not occur at about room temperature whereas it would occur at about 100°K., even after allowance is made for the widely different conditions of the glassy state and the liquid aqueous solution. We have, therefore, investigated this seeming anomaly by a tracer technique using allyl alcohol which has both α-hydrogen atoms replaced by deuterium atoms. The principle of the method depends upon the formation of deuterium-containing water by abstraction of deuterium atoms with hydroxyl radicals. In order to analyze the products of the reaction, we have developed a method based on the reaction of gaseous water with sodium mirrors. Details of this method and the determination of separation factors for protium and deuterium on solid sodium are reported here. We have also obtained some supporting evidence from electron spin resonance studies with allyl alcohol-3,3-d_2.

Experimental Section

Materials. Hydrogen peroxide (90%), Becco Chemical Division, was used without further purification. Allyl alcohol, Fisher Certified Reagent, was purified by fractional distillation. Allyl alcohol-3,3-d_2 was syn-

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