Radiolysis of Organic Compounds. V. n-Hexane Vapor

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The radiolysis of n-hexane vapor by 800 kvp. electrons gave the product-group yields G (low molecular weight) = 8.6, G (intermediate molecular weight) = 2.3 and G (dimer) = 0.4. The effect of added propylene on these yields has been examined; the dimer and intermediate group yields were decreased by about one-half while the low group was changed only slightly. These results are discussed in terms of Futrell's hydride ion transfer mechanism. In the presence of a tenfold excess of hydrogen the low and intermediate product yields were unchanged whereas the dimer yield increased threefold. Finally a brief comparison is made of the vapor phase yields and the liquid phase yields. The vapor results show a much higher proportion of products which must ultimately result from C–C bond cleavage while the liquid results show a higher proportion of product which must result from C–H bond cleavage.

Introduction

Davison[1] has reviewed the radiation chemistry of gaseous alkanes and discussed his recent work with propane. To account for the observed products and the effect of iodine on the products, he proposed a reaction scheme involving both excited and ionized molecules. According to this scheme, the low molecular weight and dimer products are formed ultimately by radical combination. Meisels, Hamill and Williams[2] have pointed out that iodine is expected to have a large electron capture cross-section and may seriously interfere with charge neutralization processes between ions and free electrons. Futrell[3] has recently studied the radiolysis of n-hexane in the vapor and liquid phase and determined the yields of hydrogen and low molecular weight products. He showed that these yields could be satisfactorily accounted for by a mechanism based on ion-molecule reactions of the hydride ion transfer type. The present paper is concerned with an examination of all the products observed in the radiolysis of n-hexane vapor, namely, low molecular weight, intermediate molecular weight and dimer products. A comparison of the vapor phase results with liquid phase results has been made and illustrates some very marked effects of phase in simple alkanes.

Experimental

The samples were irradiated with 800 kvp. electrons from a resonant transformer unit. All irradiations were made at room temperature. The irradiation cells were made of glass with a 1 mil stainless steel window attached through a Fernico seal. The liquid cell was a short cylinder 1″ in diameter and 1″ long and contained 1.0 ml. liquid. The vapor cell was a cylinder 2″ in diameter and 12″ long and was filled to a pressure of 100 mm. The liquid samples were irradiated to a total dose of 1.8 × 10^{21} eV./g. The vapor samples were irradiated to approximately the same total energy absorbed. Since precise dosimetry was not undertaken with the vapor cell, all G-values were calculated relative to the hydrogen yield using $G(H_2)$ = 5.0. The purification of the n-hexane used in these studies already has been described.[4]

After irradiation three product fractions were isolated, namely (1) liquid nitrogen volatiles, (2) −120° volatiles and (3) the remainder which was distilled into a small vial and sealed off. The liquid nitrogen volatiles were analyzed by gas chromatography with a calibrated 2-meter silica gel column, the −120° fraction was analyzed with a 2-meter didecyl phthalate column.

(1) W. H. T. Davison, Chem. Soc. (London), Spec. Publ., 9, 151 (1957).

(2) G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., J. Phys. Chem., 61, 1456 (1957).

(3) J. H. Futrell, This Journal, 81, 5921 (1959).

(4) H. A. Dewhurst, J. Phys. Chem., 62, 15 (1958).

Results and Discussion

The observed radiolysis products from n-hexane vapor are listed in Table I. The results are compared with the recent data of Futrell,[3] Back and Miller[5] and Henri, et al.[6] It should be noted that the yields reported by Futrell and by Back and Miller are initial values while the yields reported in this paper correspond to 5% reaction and the yields reported by Henri, et al., correspond to 41% reaction.

Table I

Yields of Products from the Radiolysis of n-Hexane Vapor

Product	This work	Futrell[a]	Back[b]	Henri[c]
		G, molecules/100 eV.		
H_2	5.0	4.3 ± 1.5	5.6	3.5
CH_4	0.5	0.5	0.78	0.44
C_2H_2	0.3	0.2	0.39	..
C_2H_4	1.1	1.1	1.6	0.08
C_2H_6	1.0	0.9	0.85	.90
C_3H_6	0.3	0.3	.28	.06
C_3H_8	2.3	1.4	.32	1.35
C_4H_8	0.06	0.1	..	..
i-C_4H_{10}	0.50	0.1	..	1.10 ⎫
n-C_4H_{10}	2.2	1.1	..	⎬
C_5H_{12}	0.60	0.20	..	0.23 ⎭
C_6H_{12} (trans)	.10	..	..	..
i-C_6H_{14}	.30	..	..	..
C_7	.50	..	..	..
C_8	1.10	..	..	..
C_9	0.47	..	..	..
C_{10}	.14	..	..	..
C_{11}	.10	..	..	..
C_{12}	.40	..	..	..

[a] Ref. 3, 2 Mev. electrons.   [b] Ref. 5,[210] Po 5.3 Mev. α's; [242]Cm 6.1 Mev. α's.   [c] Ref. 6, radon α source.

The yields of hydrogen, methane and C_2 hydrocarbons are in agreement with those reported by Futrell[3] and Back and Miller.[5] It is difficult to understand the low propane yield of Back and Miller particularly since the propylene yields are in good agreement. The discrepancy could be due to an effect of radiation quality but this is difficult to assess without a complete product analysis for the α-particle radiolysis. Henri, et al.,[6] found very small yields of ethylene and propylene which undoubtedly is due to the very large conversions in

(5) R. A. Back and N. Miller, Trans. Faraday Soc., 55, 911 (1959).

(6) V. P. Henri, C. R. Maxwell, W. C. White and D. C. Peterson, J. Phys. Chem., 56, 153 (1952).

their experiments. The yields of C_4 and C_5 hydrocarbons in the present work are appreciably higher than those of Futrell.

In the radiolysis of *n*-hexane vapor, the distribution and yields of higher molecular weight products than the reactant have not heretofore been reported. Although the precise nature of these products was not determined, the gas chromatographs were found to be qualitatively identical with those obtained from the radiolysis of liquid *n*-hexane.[4] Examination of this product fraction by infrared did not show any large amounts of unsaturation.

The effect of added propylene (10%) on the product yields is shown in Table II. In the presence of propylene, the hydrogen yield was decreased to 40% of the yield for pure *n*-hexane vapor and presumably represents the fraction of hydrogen formed by molecular-like reactions. Dorfman[7] has reported that at least half of the hydrogen is formed by a molecular detachment process in the radiolysis of ethane. From scavenger studies at low conversions, Back[8] has found that about one-third of the hydrogen from several gaseous alkanes is formed by molecular detachment. The methane yield was essentially unchanged in the presence of propylene suggesting a molecular process for its formation. The small increase in the ethylene yield and a corresponding decrease in the ethane yield in the presence of propylene indicates that these products are also formed largely by non-radical processes. The small increase in ethylene yield can be attributed to a protective effect of the propylene. The increased propane yield can be attributed to scavenger reactions of propylene with hydrogen atoms. The increased yield of butene, although still a very small yield, may be due to scavenger protection by the propylene. The addition of propylene had a small effect on the isobutane yield but decreased the *n*-butane yield appreciably. From the rate constant ratio for disproportionation-combination of ethyl radicals (0.14),[9] it would be expected that disproportionation of ethyl radicals would not contribute appreciably to the yield of ethylene and ethane. Pentane formation was unaffected by propylene which suggests that pentane may be formed by molecular decomposition of an excited hexane molecule. A conceivable mechanism would be the ejection of a methylene radical from an excited hexane molecule which in the presence of a large excess of hexane could lead to heptane formation by an insertion-type reaction. This speculation is qualitatively consistent with the similarity of the pentane and heptane yields for pure hexane and would explain the small increase in butene yield and small decrease in heptane yield in the presence of added propylene. The above results on the effect of propylene on the low molecular weight products are consistent with the ethylene and oxygen scavenger experiments of Futrell.[3] These results show that the low molecular weight products, with the possible exception of *n*-butane, appear to be formed largely by non-radical processes. Iodine[1] and nitric oxide[10] scavenger experi-

(7) L. M. Dorfman, *J. Phys. Chem.*, **60**, 826 (1956).

(8) R. A. Back, *ibid.*, **64**, 124 (1960).

(9) D. G. L. James and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A244**, 19 (1958).

ments in the radiolysis of propane have shown qualitatively similar results.

The yields of intermediate molecular weight and dimer products, with the exception of the C_9 product, were in general decreased in the presence of propylene (Table II). The enhanced C_9 yield can be attributed to the addition of C_6 fragments to propylene. Qualitatively, these results suggest that the intermediate and dimer products are formed, at least in part, by radical combination processes.

It was of interest to examine the effect of hydrogen in large excess (70 cm.) on the radiolysis of hexane vapor. As shown in Table II, the low

TABLE II

EFFECT OF PROPYLENE AND HYDROGEN ON THE RADIOLYSIS YIELDS FOR *n*-HEXANE VAPOR

Product	Pure *n*-hexane	Added propylene	Added hydrogen
	G, molecules/100 eV.		
H_2	5.0	2.1	..
CH_4	0.5	0.48	..
C_2H_2	0.3	0.20	
C_2H_4	1.1	1.3	2.1
C_2H_6	1.0	0.80	
C_3H_6	0.3	..	2.0
C_3H_8	2.3	3.0	
C_4H_8	0.06	0.12	
i-C_4H_{10}	0.50	0.70	2.2
n-C_4H_{10}	2.2	1.2	
C_5H_{12}	0.60	0.60	0.90
C_5H_{12} (*trans*)	.10	..	
i-C_6H_{14}	.30	0.40	0.45
C_7	.50	.40	.50
C_8	1.1	.48	.90
C_9	0.47	1.30	.60
C_{10}	.14	0.10	.21
C_{11}	.10	..	.15
C_{12}	.40	0.18	1.30

molecular weight and intermediate molecular weight product yields were not significantly affected. The dimer yield, however, was increased threefold. The unexpected large increase in dimer yield must be due to a specific effect of the added hydrogen rather than a general effect of enhanced energy absorption since the yields of other products were essentially unchanged. Thus the enhanced dimer yield could be attributed to ion molecule reactions such as

$$H_2^+ + H_2 \longrightarrow H_3^+ + H$$

followed by neutralization of H_3^+ to give three atoms which would react with hexane by abstraction to give additional hexyl radicals. The subsequent coupling of the hexyl radicals would give an increased dimer yield.

Table III shows the results for the vapor phase and liquid phase radiolysis of *n*-hexane. Futrell's[3] recent study of the liquid phase (results in Table III) was confined to the low molecular weight products. The discrepancy with Futrell's liquid phase yields for the C_2, C_3 and C_4 hydrocarbons is not understood. A comparison of the liquid phase and vapor phase results shows that the low molecu-

(10) Kang Yang and Peter J. Manno, THIS JOURNAL, **81**, 3507 (1959).

TABLE III

ELECTRON RADIOLYSIS OF n-HEXANE VAPOR, COMPARISON WITH n-HEXANE LIQUID

Product	Vapor	Liquid — This work[a]	Futrell[b]
		G, molecules/100 eV.	
H_2	5.0	5.0	4.95
CH_4	0.5	0.12	0.13
C_2H_4	1.1	.30	.63
C_2H_6	1.0	.30	.63
C_3H_6	0.3	.13	.49
C_3H_8	2.3	.42	.67
C_4H_8	0.06	.03	.46
i-C_4H_{10}	0.50	.0	< .005
n-C_4H_{10}	2.2	.50	.80
C_5H_{12}	0.60	.30	Trace
C_6H_{12}	.10	1.2	...
i-C_6H_{14}	.30	0.0	...
C_7	.50	.15	...
C_8	1.10	.53	...
C_9	0.47	.45	...
C_{10}	.14	.43	...
C_{11}	.10	.02	...
C_{12}	.40	2.0	...

[a] Ref. 4. [b] Ref. 3.

lar weight products are decreased in the condensed phase. It is of considerable interest to note that both the isobutane and isohexane products are not observed in the liquid phase. The formation of these products in the vapor phase was unaffected by the addition of propylene which suggests a molecular process. The excited state or states required for the formation of these products is evidently quenched in the condensed phase. *trans*-Hexene is an important liquid phase product whereas in the vapor phase it is only a minor product. Although a molecular process has been postulated for the formation of *trans*-hexene in the condensed phase,[4] the rather small yield in the vapor phase suggests that in the liquid phase it may be formed by a disproportionation reaction in the spurs. The C_7, C_8 and C_{11} intermediate product yields are appreciably larger in the vapor phase; the C_9 product yield is essentially unchanged while the C_{10} yield is larger in the liquid phase. The dimer yield shows a very marked effect of phase being fivefold higher in the liquid. It is of interest to compare the gross yields of low molecular weight, intermediate molecular weight and dimer products for vapor phase and liquid phase radiolysis

	Vapor	Liquid
G (C_1)	8.6 (5.9)[3]	2.1 (4.0)[3]
G (*trans*)	0.1	1.2
G (C_i)	2.3	1.6
G (C_d)	0.4	2.0

The low molecular weight product yields of Futrell[3] are shown in parentheses. The reason for the discrepancy is not understood.

The above chemical yields are undoubtedly a measure of the over-all fragmentation pattern for the liquid and vapor phase radiolysis. Although a direct comparison with mass spectral data is not possible, it is of interest to point out certain trends. The vapor results show a much higher proportion of products which must ultimately result from C–C bond cleavage while the liquid results show a higher proportionation of products which result from the parent fragment, *i.e.*, C–H bond cleavage. In this sense, therefore, the vapor phase results more closely resemble the mass spectral behavior than the liquid phase.

Futrell[3] recently has proposed a mechanism for the radiolysis of hexane based on ion-molecule reactions of the hydride-ion transfer type. He uses the mass spectral fragmentation pattern to represent the initial distribution of ions and points out the limitation of this and other assumptions in the mechanism. In general the agreement between observed and calculated yields is good even though no account is taken of the possible contribution by excitations. The theory also predicts the fractional contribution of radical reactions for each product yield. The agreement appears satisfactory except in the case of butane and pentane formation. In the case of pentane the theory predicts a radical contribution of 90% while experiment shows (Table II) that added propylene does not affect the yield. In its present form the theory predicts that the intermediate molecular weight and dimer products are formed entirely by radical combination processes. The results in Table II show that approximately one-half these products may be formed by processes other than radical combination. Therefore, the theory may require the consideration of chain-lengthening ion-molecule reactions in addition to the hydride ion transfer type.