able of being developed in a more rigorous fashion as hyperconjugation has been developed,[3e,27] but even the crude calculations seem to give an adequate measure of the Baker–Nathan effect, and they have the advantage that the method is very easily applicable to a wide variety of systems.

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(27) (a) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953); (b) Y. I'Haya, *J. Chem. Phys.*, **23**, 1165 (1955); (c) Y. I'Haya, *ibid.*, **23**, 1171 (1955).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT OF THE ATLANTIC REFINING COMPANY]

Irradiation of Petroleum Hydrocarbons. I. Electron Bombardment of Liquid Butanes[1]

BY V. J. KEENAN, R. M. LINCOLN, R. L. ROGERS AND H. BURWASSER

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The irradiation of liquid *n*-butane by 1 million volt electrons yields principally mixtures of octenes and octanes. Smaller amounts of hydrogen, ethane, butene and higher products, *i.e.*, C_{12}, C_{16} and C_{20} hydrocarbons are also encountered. Isobutane yields, in addition to such products, methane, propylene and large amounts of C_7 hydrocarbons which are attributed to the formation of C_3 fragments and their subsequent participation in addition or combination reactions. The carbon skeletons and relative amounts of the C_8 isomers have been determined but do not unequivocally indicate the manner of formation of these compounds.

Introduction

Prediction of the effect of atomic radiation upon complex hydrocarbons and their mixtures requires elucidation of mechanisms for simple hydrocarbon systems. Steacie[2] has recently reviewed the literature of free radical mechanisms. In addition, several reviews on the effect of radiation upon organic compounds have appeared.[3-5] To gain further information on the chemical nature of the liquid products we have undertaken the study of the irradiation of simple hydrocarbons. Such information is fundamental to the industrial application of atomic radiation to organic chemical reactions.

For the irradiation experiments here reported, the butanes were chosen as the simplest hydrocarbons which can demonstrate the role of primary, secondary and tertiary carbon atoms in the reaction mechanism. A one-million volt electron accelerator was chosen for its high and alterable energy as well as its experimental convenience.

Experimental

The equipment consisted of two parts: the electron accelerator and an enclosed system for circulating liquid butane and exposing it to the electron beam. The accelerator was a General Electric Company Resonant Transformer,[6] operating at 1 mev. and 0.2 to 1.0 ma. beam out.

The chemical reaction system comprised a reaction cell equipped with a circulating pump, Dry Ice condensers and cooling coil, and reservoirs for the removal of samples and addition of reactants. Initial irradiations of *n*-butane were carried out using a conventional centrifugal pump which required correction of experimentally determined values to compensate for leakage. Later irradiations of *n*-butane and the first irradiations of isobutane were performed using various capacity diaphragm pumps. These were troublesome because of "vapor lock" and their low rate of flow (up to 0.2 liter per min.) which to avoid overheating the butane, limited the maximum current of the electron beam to 0.4 ma. Finally, a Chempump model E proved satisfactory for leak-proofness and capacity.

The condensers, reservoir, thermocouple well and sampling pot were all of Pyrex, fitted together by ground glass joints. The tubing and coil were of copper, the pump of stainless steel, and the valves, tubing fittings and irradiation cell were of brass. Metal to glass connections were made by means of ground semi-ball joints.

The irradiation cell (Fig. 1) was a shallow brass cylinder with an internal diameter of 3 in. and an internal height of $^{5}/_{16}$ in. which when filled with liquid hydrocarbon was sufficient to absorb virtually all of the electrons entering the system. The maze absorbed only 15% of the radiation while providing more uniform irradiation of the flowing liquid sample. The cell outlet was located at the upper edge to permit gases to escape while maintaining the cell filled with liquid. A 2 mil stainless steel disc provided a cover for the cell through which 90% of the electron energy passed. The base of the cell contained an integral cooling chamber through which a Dry Ice–alcohol solution was circulated. A clamping ring and through-bolts held the assembly together.

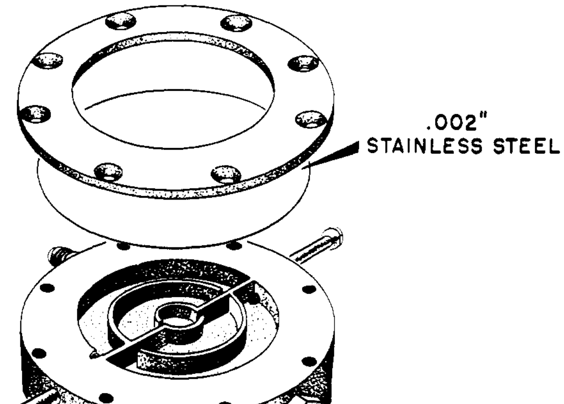

Fig. 1.—Irradiation cell.

The reaction system, including the irradiation cell and the Chempump had a capacity of about 1200 ml. of liquid. Residence times, under the electron beam, could be varied between 5 and 50 seconds per pass when using the Chempump. Reaction temperatures were maintained at −30 to −50° by circulating the butanes through the Dry Ice-cooled coil in series with the reaction cell. A thermocouple was located in the effluent from the cell to measure the temperature. Gases formed during the irradiation were led through a Dry Ice condenser and thence through a sampling manifold to a gas meter.

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(1) Presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

(2) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954.

(3) E. Collinson and A. J. Swallow, *Chem. Revs.*, **56**, 471 (1956).

(4) B. M. Tolbert and R. M. Lemmon, *Radiation Research*, **3**, 52 (1955).

(5) H. K. Sun, *Modern Plastics*, **32**, 1, 141 (Sept. 1954).

(6) J. A. Knowlton, G. R. Mahn and J. W. Rantfl, *Nucleonics*, **11**, 64 (1953).

Irradiation times up to 5.5 hours were employed. At this maximum time, approximately 22 wt. % of the initial 450 g. of *n*-butane was converted into products. This is a dosage of 1.5×10^9 rep., corresponding to 1500 watt hours or 32×10^{24} electron volts. Dosages were based on calorimetric calibration of the accelerator beam with a 2 mil stainless steel foil interposed to simulate the irradiation cell cover. These calorimetric measurements were checked against a calibration using a standard ionization chamber, and from the accuracy of measurements and reproducibility have a probable error of ±2%.

Samples of the irradiated butanes were separated into a butane and lighter gas and a hexane and heavier liquid by distillation through a Podbielniak column. The gas samples were analyzed in a Consolidated Engineering Corp. model 21-101 (modified) mass spectrometer. The liquid samples were analyzed in a Consolidated Engineering Corp. model 21-103 mass spectrometer with a heated inlet to assure complete volatilization of the samples. Analysis of the liquid samples was judged accurate to ±2% absolute.[7] The gases were determined with an accuracy of 1% (absolute).[8]

To determine the C_8 hydrocarbon chain structures, samples of the heavier liquid fractions from several dosage levels were combined, hydrogenated at 50 p.s.i.g. and 50° for one hour. The products were distilled at 5:1 reflux ratio through a 5 mm. diameter, 1 m. long, spiral wire packed column having a theoretical efficiency of 50 plates at total reflux. The fraction boiling from 114 to 126° was used for determination of the C_8 isomers from *n*-butane while the fraction 95° to 129° was used for determination of the C_8 isomers from isobutane. It was estimated that this hydrogenation and distillation introduced an error no greater than ±5% (absolute).

Results and Discussion

Direct Products of the Irradiation.—Electron bombardment of liquid *n*-butane at −30 to −50° in a continuous flow, recycle apparatus yields principally hydrogen butene and octenes, as shown in Table I from which the *G*-values can be readily computed.

In contrast, isobutane yields under the same conditions much more methane and propene as well as large amounts of C_7 hydrocarbons, as shown in Table II.

Because of the high degree of branching in the isobutane products of higher molecular weight, it is more difficult to distinguish the components of such a mixture by mass spectrometric techniques. Therefore, distillation was employed to distinguish among the products, albeit with less accuracy. Any C_6 hydrocarbons present cannot be determined by this technique since they are inevitably lost in the distillation of the very large amount of isobutane.

Variations in the amounts of the major products from the irradiation of *n*-butane with energy absorbed are shown in Fig. 2. The decrease in rate of butene formation suggests that it is being consumed to form other products. The apparent increase in rate of formation of C_8 compounds when the rate of butene formation begins to decrease suggests that the butene is being consumed in the formation of C_8 compounds. This may also explain the preponderance of octenes in the C_8 fraction. Since the rate of formation of C_{12} products does not appear to increase in proportion to the concentration of C_8 products it may be concluded that C_{12} compounds are formed not from the C_8 compounds but rather by an alternate route, perhaps from a precursor of the C_8 compounds.

TABLE I

PRODUCTS OF *n*-BUTANE IRRADIATION WITH 1 MEV. PEAK ELECTRONS AT −30°

	Amount of product in centimoles ± 2			
Time, min.	28	132	190	334
Energy absorbed $\times 10^{-24}$, e.v.	2.7	13	18	32
Hydrogen	5	27	42	72
Methane	1	4	5	7
Ethene	3	5	5	5
Ethane	11	20	30	20
Propene	3	6	11	4
Propane	7	8	6	7
Butene	6	18	29	26
Pentane	3	3	4	3
Hexane	1	5	...	....
Heptane	0.3	0.7	...	....
Octene	3	13	28	49
Octane	1.5	4	10	13
Nonane	0.1	0.3	...	....
Decane	0.1	0.3	...	....
Dodecadiene	...	....	2.5	1.4
Dodecene	0.4	2.6	7	6
Dodecane	...	0.2	...	0.3
Hexadecadiene	...	....	0.7	0.7
Hexadecene	0.1	0.8	1.8	1.3
Hexadecane	0.1	0.5	...	0.7
Eicosadiene	...	....	0.2	0.2
Eicosene	0.04	0.1	0.5	0.3
Eicosane	0.04	0.03	...	....
Tetracosadiene	...	....	0.1	0.1
Tetracosene	...	0.1	...	....
Octacosadiene + octacosene	...	....	0.1	0.1
Dotriacontadiene + other C_{32}	...	....	0.1	0.05

TABLE II

PRODUCTS OF ISOBUTANE IRRADIATION WITH 1 MEV. PEAK ELECTRONS AT −30°

Energy absorbed $\times 10^{-24}$, e.v.	Amount of product in centimoles ± 2				
	4.8	0.6	14.4	19	23
Hydrogen	14	26	39	52	63
Methane	5	10	16	21	27
Ethene	0.5	1.4	2	3	4
Ethane	8	4	5	8	7
Propene	9	12	18	24	22
Propane	3	18	9	12	4
Isobutene	6	12	13	17	17
Pentane	2	4	7	13	12
C_6 compounds	Not determined				
C_7 compounds	2.3	5.5	9.3	10	13
C_8 compounds	1.0	5.5	4.4	4.6	6.1
$>C_8$ compounds[a]	3.3	9.1	12	13	16

[a] Calcd. on C_{12} basis.

Variations in the amounts of the major products from the irradiation of isobutane with energy absorbed are shown in Fig. 3. These irradiations were not continued as long as the irradiations of *n*-butane. There is, here, little evidence for a maximum rate of formation of C_7 or C_8 compounds although the olefins apparently reach maximum concentrations at the same extent of irradiation as was noted in the case of *n*-butane. The large amounts of C_7 compounds indicates that propene may be entering into their formation.

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(7) R. A. Brown, R. C. Taylor, F. W. Melpolder and W. S. Young, *Anal. Chem.*, **20**, 5 (1948).

(8) H. W. Washburn, H. F. Wiley and S. M. Rock, *Ind. Eng. Chem., Anal. Ed.*, **15**, 541 (1943).

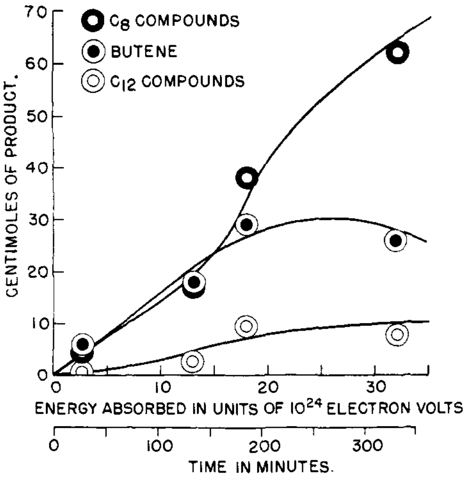

Fig. 2.—The higher molecular weight products of *n*-butane irradiation *versus* energy absorbed or time.

These phenomena may be explained by the following reaction scheme, wherein R may vary from reaction to reaction.

Typical primary processes may be represented by

$$RR_1 \rightsquigarrow R + R_1 \qquad (1)$$

$$RCH_2CH_2R_1 \rightsquigarrow RCH = CHR_1 + H_2 \qquad (2)$$

$$RR_1 + R_2R_3 \rightsquigarrow RR_2 + R_1R_3 \qquad (3)$$

where R and R_1 represent ionic and/or radical species in all energy states. The lighter of these species, *e.g.*, H, CH_3, C_2H_5 and C_3H_7 are most apt to have excess kinetic energy.

The chain propagating steps may be represented by

$$R^* + C_4H_{10} \longrightarrow RH + C_4H_9 \qquad (4)$$

$$C_nH_{2n} + R \longrightarrow C_nH_{2n-1} + RH \qquad (5)$$

$$C_nH_{2n} + R \longrightarrow C_nH_{2n}\,R \qquad (6)$$

Since the concentration of radicals is relatively low and that of butane high, the most likely reaction for "hot" radicals (R*) is abstraction of hydrogen from the butane (reaction 4), thus effectively converting the more excited, lighter radicals to butyl radicals. At the reaction temperatures which we employed (−30 to −50°) it is not expected that hydrogen abstraction would take place to a great extent when the attacking radical does not possess excess kinetic energy. The site of the hydrogen abstraction, in the case of excited attacking radicals, will not be influenced appreciably by the relative strengths of 1, 2 or 3° C–H bonds. Therefore, unlike the thermal decompositions of butanes,[9] the ratios of primary to secondary butyl radicals and primary to tertiary isobutyl radicals will not necessarily correspond to the thermodynamic equilibrium.

Abstraction of hydrogen from an olefin (reaction 5) is favored by the lability of allylic hydrogens, and it is expected that this reaction will take place with unexcited radicals. The olefin radicals thus formed are stabilized by resonance in the same way as radicals formed from propylene.[2] This stabilization gives these radicals a concentration, relative to butyl radicals, far out of the proportion of butene to butane, and thus these radicals play a much greater role than would otherwise be expected. These radicals will not have sufficient energy, in general, to abstract hydrogen as in reactions 4 and 5, nor will they generally be able to form the less stable radical by addition to an olefin as in reaction 6. However, they will undergo radical combination with each other or other radicals (reaction 7) and may occasionally disproportionate with reactive radicals (reaction 8).

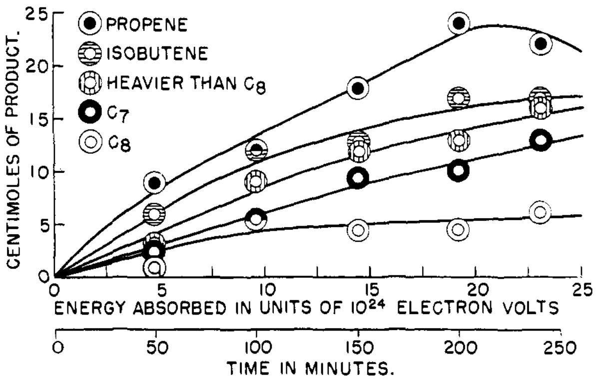

Fig. 3.—The higher molecular weight products of isobutane.

Addition of a radical to an olefin (reaction 6) is in competition with the abstraction of hydrogen from the olefin (reaction 5) as indicated in the data of Cramer.[10] This addition product will then disproportionate to yield octene and octane, or it may also combine with butyl radicals, allylic radicals or octyl radicals to yield the higher molecular weight products.

The chain terminating steps are

$$R + R_1 \longrightarrow RR_1 \qquad (7)$$

$$C_nH_{2n+1} + R \longrightarrow C_nH_{2n} + RH \qquad (8)$$

It will be noted that a higher per cent. of paraffins was encountered in our work, among the C_8 products, in the initial stages. This suggests that saturated radical combination (reaction 7), over and above primary processes (reaction 3), accounts for a greater proportion of the higher molecular weight products in the initial stages of the irradiation than addition of a radical to an olefin (reaction 6) or combination of allylic radicals (reaction 7). However, as olefin concentration builds up, by disproportionation (reaction 8) or by a molecular process (reaction 2) reactions 5 and 6 may become more important, resulting in more olefin among the heavier products.

Structure of the Octanes.—To gain more information on the species and reactions contributing to the formation of C_8 compounds from irradiation of *n*-butane and isobutane the carbon skeleton of the C_8 compounds was investigated. The products of a series of irradiations were combined, hydrogenated, and the octanes carefully separated from the other products by fractional distillation. Mass spectrometric analysis of the octane fraction yielded the following data.

n-Butane irradiation produced *n*-octane, 17%; 3-methylheptane, 45%; 3,4-dimethylhexane, 34%; 2,3-dimethylhexane,[11] 4%; and 3-methyloctane, 0.3%. Isobutane produced 2,5-dimethylhexane,

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[9] R. N. Pease and E. S. Durgan, THIS JOURNAL, **52**, 1262 (1930).

[10] P. L. Cramer, *ibid.*, **60**, 1406 (1938).

[11] Formation presumably involves isomerism of the carbon chain.

TABLE III

RATIO OF PRIM. *n*-BUTYL TO SEC. *n*-BUTYL FOR VARIOUS MODES OF C_8 FORMATION

Mode of formation	Range of ratios of prim. to sec. butyl radicals[a]	Predicted ratio of C_8 isomers[b]	Compd. accounted for
A	0.54:1 to 0.9:1	12:46:42 to 22:50:28	Saturated C_8
B	All values[c]	12:46:42[d] to 22:50:28[e]	Unsaturated C_8
C	0.24:1[f] to 1.5:1[g]	11:54:35 to 18:54:28	Unsaturated C_8, saturated and unsaturated C_{12}, C_{16}, etc.
D	0.24:1[h] to 1.5:1[i]	11:54:35 to 18:54:28	Unsaturated C_8
E	Not pertinent	36:48:16[j]	Saturated C_8

[a] These are actually ratios of (concentration times reactivity). [b] Values given are *n*-octane, 3-methylheptane, 3,4-dimethylhexane. The maximum deviation from the experimental values 18:35:47, which was considered was ±7, made up of ±2 analytical error and ±5 handling and distillation error. [c] All methods of formation of the allylic radical produce the resonant form. [d] The corresponding required ratio of the reactivities of the 1- and 3-positions of the allylic radical is 0.54:1, respectively. [e] The corresponding required ratio of reactivities of the 1 and 3 positions of the resonant allylic radical is 0.9:1, respectively. [f] Assymetric addition to the double bond by the ratio 1.3:1 favoring less branching yields this minimum value. The corresponding required ratio of butene-1 to butene-2 is 00:1. [g] Asymmetric addition to the double bond only reduces this limit. The corresponding ratio of butene-1 to butene-2 is 1.5:1. [h] The corresponding required ratio of reactivities of the 1- and 3-positions of the resonant allylic radical is 1.3:1, respectively. [i] The corresponding required ratio of reactivities of the 1- and 3-positions of the resonant allylic radical is 0.43:1, respectively. [j] Based on equal probability for removal of any two hydrogens.

42%; 2,2,4-trimethylpentane, 45%; 2,2,3,3-tetramethylbutane, <3%; 2,4-dimethylhexane,[11] 12%; and 2,3,3-trimethypentane,[11] 1%.

Omitting the isomerization products and the C_9 product, the ratios of the C_8 isomers found from *n*-butane are: *n*-octane, 18; 3-methylheptane 47; 3,4-dimethylhexane 35. From isobutane the ratios are: 2,5-dimethylhexane 47; 2,2,4-trimethylpentane, 51; 2,2,3,3-tetramethylbutane 2 ± 2.

While these results do not provide complete elucidation of the importance of the various reactions and the degree of equilibrium attained between primary and secondary *n*-butyl radicals or primary and tertiary isobutyl radicals, they do permit some general relationships to be developed.

The various modes of formation of C_8 compounds are

A. Combination of butyl radicals (reaction 7)
B. Combination of allylic radicals (reaction 7)
C. Addition of butyl radicals to butene (reaction 6)
D. Reaction of allylic radicals with butyl radicals (reaction 7)
E. Primary bimolecular process (reaction 3)

Assuming, in turn, that each of these accounted for all the C_8 formed, the lower and upper limits of the ratio of the isomeric butyl radicals which will permit the isomeric C_8 products to be formed in the ratio observed, have been calculated. The results for *n*-butane and isobutane are shown in Tables III and IV, respectively.

TABLE IV

RATIO OF PRIM. ISOBUTYL TO TERT. ISOBUTYL FOR VARIOUS MODES OF C_8 FORMATION

Mode of formation	Range of ratios of prim. to tert. isobutyl radicals[a]	Predicted ratio of C_8 isomers[b]	Compd. accounted for
A	2.2:1	47:43:10[c]	Saturated C_8
B	All values	100:0:0[c]	Unsaturated C_8
C	0.7:1 to 1.4:1	40:58:2[d] to 52:44:4[e]	Unsaturated C_8
	9:1 to 00:1	52:44:4[f] to 48:52:0	Saturated and unsaturated C_{12}, C_{16}, etc.
D	0.7:1 to 1.2:1	42:58:0 to 54:46:0	Unsaturated C_8
E	Not pertinent[g]	56:38:6 to 81:18:1	Saturated C_8

[a] These are actually ratios of (concentration times reactivity). [b] Values given are 2,5-dimethylhexane:2,2,4-trimethylpentane:2,2,3,3-tetramethylbutane. The maximum deviation from the experimental values of 47:51:2 which was considered was ±7 for the first 2 figures and ±2 for the third. [c] Although these values are not within ±7 of the experimental this is the closest approach which can be made. [d] The addition to the olefin must be 35:1 in favor of the less substituted product to achieve this minimum ratio. [e] The addition to the olefin must be 8:1 in favor of the less substituted product to achieve this maximum ratio. [f] The addition to the olefin must be 1.4:1 in favor of the less substituted product at this extreme. [g] The calculations are made by assuming in turn (1) an equal probability of a linkage occurring between any two carbon atoms selected one from each of two adjacent molecules, (2) an equal probability of a linkage occurring between any two hydrogen atoms selected one from each of two adjacent molecules with simultaneous linking of the carbon atoms from which the hydrogens came.

The total reaction mechanism in all probability is made up of contributions of all these modes. The additional functions expressing the contribution of each mode cannot, from these data, be unraveled. Thus, we are unable to define the limits of the ratios of primary to secondary *n*-butyl radicals, or primary to tertiary isobutyl radicals.

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