

about four thousand.<sup>23</sup> On this basis, molecular weights have been computed from the diffusion coefficients shown in Fig. 1 and the resultant estimated molecular weight distribution curves are illustrated in Fig. 2.

(23) These constants for the molecular weight-diffusion coefficient exponential relationships were obtained with fractions prepared by a previously described procedure<sup>4</sup> using weight average molecular weights which were estimated previously by a light scattering procedure<sup>4</sup> and using weight average diffusion coefficients which have recently been newly determined in the presently used buffered 1 M NaCl solution.

Although rather accurate measurements and calculations are necessary for satisfactory estimation of distributions, it appears that approaches of the above-described type often may be found useful in studies of polymers. Kinetic studies of changes in distributions of diffusion coefficients for lignin sulfonates are proceeding utilizing the described theory and methods.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, AND SHELL DEVELOPMENT COMPANY]

## Direct Dimerization of Terminal Olefins by Ionizing Radiation<sup>1,2</sup>

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Terminal olefins were irradiated in liquid phase with high energy electrons and  $\gamma$ -rays to study the mechanism of radiolysis. Low molecular weight polymers were the principal products. The dimeric fraction was mainly monoolefin, with small amounts of diolefins, paraffins and cyclic material. Hydrogenation of the dimer yielded *n*-dodecane (45%) and 5-methylundecane (35%). Ozonolysis of the dimer fraction and identification of the isolated acids provided a pattern consistent with the location of the double bond in any of several of the possible locations in the simple carbon skeletons. The contrast between these structures and those obtained in free radical-induced reactions of terminal olefins provides evidence against a free radical mechanism. An ion-molecule mechanism is proposed to explain these facts; it is postulated that the molecule ion reacts directly with a molecule to form a carbon-carbon bond utilizing the pi electrons of the molecule. The energy-rich complex so formed is held together in the liquid cage until its energy is dissipated by collision.

Although the nature of the fundamental processes in the radiolysis of saturated hydrocarbons has been investigated in some detail, that of simple olefins has received little attention. Both free radicals<sup>3-6</sup> and ions<sup>7-11</sup> have been suggested as intermediates in the radiolysis of paraffins. In order to investigate the relative importance of these intermediates in the radiolysis of simple olefins, 1-hexene and 1-octene have been irradiated and the products analyzed and compared with those obtained from radical-induced reactions of simple olefins.<sup>12,13</sup>

### Experimental

**Purification of Starting Materials.**—The olefins (Pure Grade, 99 mole % minimum, Phillips Petroleum Co.) were fractionally distilled over sodium under nitrogen. The

purified olefins did not give a test for peroxides. The 1-hexene contained 0.01% *n*-hexane plus 0.06% other unidentified hydrocarbons.

**Irradiation with  $\gamma$ -Rays.**—The source of  $\gamma$ -rays was the High Level Irradiation Facility of the Argonne National Laboratory. The olefin was thoroughly degassed under vacuum, distilled into a 200-ml. irradiation flask, and the flask was sealed *in vacuo*. Radiation dosage was determined by ferrous sulfate dosimetry.

**Irradiation with Electrons.**—The source of electrons was a 3 Mev. Van de Graaff accelerator. Irradiation was conducted in an all-glass apparatus consisting of an irradiation cell with 1 mm. thick window, a reservoir, a  $-78^\circ$  reflux condenser and a gas collector. The capacity of the system was 150 ml. The olefin was circulated through the irradiation cell by a magnetic centrifugal pump, and the olefin was cooled by a heat exchanger in the circuit. The beam current used was 3 microamperes. Dosage was determined by ceric ion dosimetry with the identical experimental arrangement. Dimensions were such that the electron beam was completely absorbed in window plus fluid.

**Analysis.**—In the electron irradiation experiments, the gaseous products collected were analyzed by mass spectrometry. In the  $\gamma$ -ray irradiation experiments, the gaseous products were removed on a vacuum line and analyzed according to the procedure used by Kharasch, Lewis and Reynolds.<sup>14</sup>

The remainder of the reaction mixture was distilled at 100 mm. and room temperature. The fraction thus collected in the Dry Ice trap was further fractionated through a Podbielniak Hyper-Cal column. The 2% forecut and the remainder were separately analyzed by gas chromatography with a dimethyl sulfolane column ( $50' \times 1/4''$ ) for the detection of C<sub>5</sub> and C<sub>7</sub> hydrocarbons, hexane, hexadienes and 2- and 3-hexenes.

The high-boiling material was distilled through a tantalum spiral column ( $24' \times 1/4''$ ). These several fractions were collected: fraction I, b.p. 87–92° (20 mm.),  $n_{20}^D$  1.4350, mol. wt., 169; fraction II, b.p. 76–80° (0.1 mm.),  $n_{20}^D$  1.4490, mol. wt., 250; fraction III, b.p. 117–120° (0.05 mm.),  $n_{20}^D$  1.4572, mol. wt., 330. The fractions were confirmed by mass spectrometric analyses to be dimers, trimers and tetramers, respectively.

(1) (a) This work was supported in part by the United States Air Force under contract with the University of Chicago (Contract No. AF 33(616)-3875) monitored by Aeronautical Research Laboratory (WCRR) Wright Air Development Center. (b) Presented at the 134th Meeting of the American Chemical Society, Chicago, Illinois.

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TABLE I  
 PRODUCTS OF OLEFIN IRRADIATIONS

Feed	Energy from	Dose rate, e.v./g. min.	Total dose, e.v./g.	<i>G</i>					
				-M	Gas	Satd. monomer	Dimer	Trimer	Tetramer
1-Hexene	Electrons	$1.88 \times 10^{20}$	$4.7 \times 10^{21}$	10.5	0.9	0.1	1.0	0.76	0.22
1-Hexene	$\gamma$ -Rays	$1.0 \times 10^{18}$	$4.1 \times 10^{21}$	18	.8	.2	1.9	.8	.7
1-Hexene	$\gamma$ -Rays	$1.0 \times 10^{18}$	$7.5 \times 10^{10}$	16	.7	.1	1.6	.7	.66
1-Hexene	$\gamma$ -Rays	$6.3 \times 10^{17}$	$2.2 \times 10^{20}$	16	.8	.3	1.8	1.0	.66
1-Octene	$\gamma$ -Rays	$1.38 \times 10^{18}$	$1.31 \times 10^{21}$	16	.6		2.0	0.9	.6

**Investigation of the Dimeric Fraction.**—The isolated dimer was examined by both infrared and mass spectrometric analysis. Various gas chromatographic columns were used in attempts to resolve it into pure components, without success.

In order to obtain information on the carbon skeleton, the dimer fraction (4.05 g.) was hydrogenated in ethanol over platinum oxide. The hydrogen uptake corresponded to  $1.0 \pm 0.05$  double bonds per molecule. The mixture of the hydrogenated dimers was examined by gas-liquid chromatography and mass spectrometry of separated fractions.

In order to obtain information about the location of the double bond, a solution of the dimer in dry ethyl acetate (1.102 g. in 100 ml.) was treated with ozone in oxygen at  $-50^\circ$ . The amount of ozone consumed corresponded to  $1.0 \pm 0.05$  double bonds per molecule. The ozonides were decomposed by catalytic hydrogenation in ethanol. The hydrogen uptake corresponded to 85% of the theoretical amount. The aldehydes were oxidized by refluxing with the stoichiometric amount of freshly-prepared silver oxide for 8 hr. The filtrate was distilled, the distillate was treated with 2,4-dinitrophenylhydrazine, and the products were separated by adsorption chromatography on silicic acid. The acetone derivative constituted more than 90% of the total. The less-volatile distillation residue was passed through activated alumina and examined by gas chromatography and mass spectrometry.

The solid silver salts collected in the filtration were converted to free acids by stirring with hydrogen chloride in ether. The acids were partitioned on a silicic acid-methanol column with iso-octane as the mobile phase,<sup>15</sup> in order to remove interfering dicarboxylic acids. Closely associated bands were collected, titrated with sodium ethoxide, the sodium salts converted to silver salts and the silver salts converted to methyl esters with methyl iodide. The methyl esters were analyzed by gas chromatography with a polypropylene glycol column and a silicone oil column. The esters were identified by their retention times, and, where necessary, by mass spectrometry. Easily identified were methyl acetate, propionate, *n*-butyrate, *n*-valerate, hexanoate, heptanoate, octanoate, decanoate and succinate. In addition, there appeared to be esters of branched C<sub>7</sub> and C<sub>8</sub> acids. The former is thought to be methyl 2-hexanoate, for the largest ion intensity in the mass spectrum above  $m/q = 44$  was that at  $m/q = 88$ . This is characteristic of  $\alpha$ -methyl methyl esters. The latter did not exhibit this peak and is therefore not the ester of an  $\alpha$ -methyl-C<sub>7</sub> acid, though it is clearly an ester of a branched C<sub>8</sub> acid.

**Investigation of the Trimeric and Tetrameric Fractions.**—Hydrogenation of the respective fractions was carried out in propionic acid (Eastman White Label) over Adams catalyst. The amount of hydrogen consumed corresponded to 0.80 and 0.75 double bond per molecule of the trimer and tetramer, respectively. Ozonizations were carried out in the manner described previously. The amounts of ozone consumed agreed with the hydrogenation data. On the other hand, mass spectra of the dimer, trimer, tetramer and pentamer gave ion intensity ratios at  $m/q = 14n - 2$  to  $m/q = 14n$  of 0.13, 0.34, 0.62 and 1.3, respectively, indicating significantly greater diolefin or cyclic olefin content as the molecular weight increases.

**Preparation of 5-Methylundecane.**—A solution of 2-octanone in dry ether was added dropwise to a refluxing ethereal solution of *n*-butylmagnesium bromide. After hydrolysis the methylbutylhexylcarbinol was isolated from the organic layer, b.p. 87–88° (0.1 mm.). Dehydration of

the carbinol with excess phosphorus pentoxide yielded a mixture of olefins which were catalytically hydrogenated. Fractional distillation of the hydrogenation product through the tantalum spiral column yielded 5-methylundecane, b.p. 91° (18 mm.),  $n_D^{20}$  1.4220. No olefinic absorption was observed in the infrared spectrum.

*Anal.* Calcd. for C<sub>12</sub>H<sub>26</sub>: C, 84.61; H, 15.39. Found: C, 84.85; H, 15.39.

**Molecular Orbital Calculations.**—Calculations made were based on the original suggestion of Hall<sup>16</sup> that there be associated with saturated carbon atoms a pseudo- $\pi$ -orbital carrying two electrons. The usual secular equation was set up, employing two different Coulomb integrals,  $\alpha_u$  and  $\alpha_s$ , for carbon atoms at the double bond and for saturated carbon atoms, respectively, and three different exchange integrals,  $\beta_s$ ,  $\beta_u$ , and  $\beta_{su}$  for interactions between saturated carbons, doubled bonded carbons, and between saturated and double-bonded carbons, respectively. The values for  $\alpha_s$  and  $\beta_s$  were taken to be 13.00 and 1.35 e.v., respectively, derived from Watanabe's<sup>17</sup> measurements of the ionization potentials of methane and ethane. The values for  $\alpha_u$  and  $\beta_u$  were taken to be 6.71 and 3.31 e.v., respectively, derived from the ionization potential of ethylene (10.52 e.v.) and N  $\rightarrow$  V transition (1625 Å. or 7.62 e.v.). The mixed exchange integral  $\beta_{su}$  was evaluated from the ionization potential for propylene and the above values; solution of the secular equation gave  $\beta_{su} = 2.44$  e.v. Validity of the calculation is supported by very good agreement (within 1%) between calculated and observed energy of the N  $\rightarrow$  V transition in propylene, 7.13 e.v.

The secular equation for 1-butene, set up and solved using the above constants, gave four orbitals with energy levels of -2.5978, -9.6151, -12.3148 and -14.8922 e.v. The latter three are filled in the molecule, but the orbital of energy -9.6151 has only a single electron in the molecule ion. Addition of the squares of the coefficients of the orbitals at each atom, for each electron occupying the orbitals, gives the charge densities quoted in the text.

## Results

Basic analytical data for the various irradiations are given in Table I.

**Gaseous Products.**—The gas produced was nearly all hydrogen; *G*-values for other gaseous products are estimated to be 0.02 for methane and acetylene, and 0.004 for ethane, ethylene, propane and propylene. No other fragmentation products were observed.

**C<sub>6</sub> Products.**—In the C<sub>6</sub> fraction, from 1-hexene, a small amount of *n*-hexane was found, as shown, but C<sub>5</sub> and C<sub>7</sub> compounds, and 2- or 3-hexenes were absent (<0.05%, or *G* = <0.1).

**Dimer.**—The dimeric fraction by gas chromatography was shown to contain more than ten components, all incompletely resolved. The mass spectrum showed it to consist of about 90% mono-olefins with a small amount of diolefin and some saturated hydrocarbon. The saturated fraction amounted to about 7–8%, estimated from the

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amount which resisted ozonolysis. From its mass spectrum it appeared to contain much cyclane, as shown by the fact that the ion intensity at  $m/q = 168$  was 1.66 times that at  $m/q = 170$ . The fragmentation pattern showed the presence of  $C_4$  branches. All of the saturated hydrocarbon was branched, since its retention time was less than that of *n*-dodecane.

The carbon skeleton of the dimeric fraction was investigated by gas chromatography of the hydrogenation product. It was shown to consist of two major components, one of them giving a completely isolated peak, the other giving a large peak superimposed on a broad range of peaks from other materials. The retention times of these two major peaks coincided with those of authentic *n*-dodecane and 5-methylundecane, respectively. The identities of these compounds were confirmed by mass spectral analyses of the separated fractions. A sample of the suspected *n*-dodecane had a mass spectrum identical with that of authentic material. Samples were collected of one forecut of the suspected 5-methylundecane, of the major fraction itself and of two cuts between the two major peaks, and these were designated cuts 1-4, respectively. The mass spectra were compared with that of 5-methylundecane, as shown in Table II.

TABLE II

MASS SPECTRA OF HYDROGENATED DIMER FRACTIONS  
ION INTENSITIES RELATIVE TO PARENT

$m/q$	5-Me-undecane	Cut 1	Cut 2	Cut 3	Cut 4
170	1.00	1.00	1.00	1.00	1.00
168	0.005	0.007	0.07	1.85	1.48
155	.28	0.21	.23	0.23	0.01
141	.49	1.43	.81	1.40	.21
140	.48	1.55	.85	2.06	.27
127	.36	0.62	.34	0.41	.34
126	.50	1.01	.58	0.92	.74
113	1.20	1.21	1.25	1.18	.44
112	2.12	2.19	2.30	2.74	1.01
99	0.49	0.62	0.40	0.78	0.51
98	0.71	0.36	0.28	1.62	1.04

While the separations were not complete, conclusions can be drawn, utilizing these three general observations regarding alkane mass spectra: (1) branched alkanes break predominantly the bonds to the tertiary or quaternary carbons, to give the fragment ions; (2) normal alkanes have very small intensities corresponding to fragment ions with loss of methyl and increasingly larger intensities corresponding to loss of ethyl, *n*-propyl, *n*-butyl, etc.; (3) intensity of the ion at  $m/q = 14n$  where  $n$  is the number of carbon atoms in the alkane is about 1% of that of the parent ion (notable single exception in the octanes, 2,5-dimethylhexane, where it is 40% of the parent). It is seen that the peak at  $m/q = 168$  rises to a large maximum at cut 3, indicating that cuts 3 and 4 are no doubt rich in cyclane. Cut 4 contains essentially no methyl or ethyl groups, as shown by  $m/q$  at 155 and 141. Cuts 2 and 3, on the other hand, contain ethyl branches, and

cut 2 appears to have some, by comparison with 5-methylundecane. Propyl branching appears to be present in cut 1 also. It should be noted that cuts 1, 2 and 3 all have the large characteristic intensity at  $m/q$  of 113, corresponding to removal of a *sec*-butyl or *n*-butyl group.

It is concluded that the mass spectrum of cut 2, the heart cut, resembles closely the mass spectrum of 5-methylundecane and that in fact the second major GLC peak must actually be due to that compound. Since it is not quite pure, it is believed to be superimposed on an unresolved mixture of minor components, the lower boiling ones having the ethyl and propyl branches typical of allylic radical condensations, the higher boiling ones having cyclic character. The over-all composition of the hydrogenated dimer, based on the relative areas, is *n*-dodecane, 45%, 5-methylundecane, 35%, and other branched and cyclic dodecanes, 20%.

Information on the nature of the double bonds of the dimer was obtained from the infrared spectrum. They appeared to be 27% vinyl, 57% *trans*-vinylene and 3% vinylidene, with the rest presumably *cis*-vinylene or tri- or tetra-substituted types.

Ideas as to location of the double bond and also the nature of the carbon skeleton were obtained from the degradation by ozonolysis. Results were consistent with location of the double bond at any of several places in *n*-dodecane and 5-methylundecane skeletons. The absence of a branched-chain  $C_9$  or  $C_{10}$  acid indicates the absence of 5-methyl-8-undecene and 5-methyl-9-undecene, but the branched  $C_7$  and  $C_8$  acids found are consistent with the occurrence of 5-methyl-6-undecene and 5-methyl-7-undecene.

**Polymers.**—Because of the inconveniently high molecular weights, the trimers and tetramers from 1-hexene were investigated only for the extent of unsaturation. Hydrogenation and ozonization data indicated the presence of less than one double bond per molecule. Mass spectral analyses, however, showed a slight apparent increase in unsaturation (or cyclization) with molecular weight. Similar results were obtained on the polymeric products from the radiolysis of 1-octene.

### Discussion and Mechanism

The present experimental results of the radiolysis of terminal olefins are in direct contrast with the results of the radical-induced reactions of terminal olefins<sup>12</sup> and with the results of the radiolysis of paraffins. Terminal olefins in free radical reactions rearrange to non-terminal olefins and give dimers containing two double bonds resulting from dimerization of allylic free radicals. On the other hand, in the radiation-induced reactions of terminal olefins, rearranged monomers are not detected and the major portion of the dimeric fraction contains only one double bond. This marked difference provided evidence against a free radical mechanism. Paraffins upon irradiation give high yields of hydrogen, olefins, fragmentation products and dimers with complicated carbon skeletons, whereas terminal olefins under similar conditions give lower yields of hydrogen, practically no fragmentation products and dimers with simple carbon skeletons. This differ-



narly does not dissociate in liquid phase. It is to be noted that the only saturated hydrocarbons resulting from reactions 2 or 3 are branched and, in some cases, cyclic. This is in accord with the results: the ozone-resistant dimer contained no *n*-dodecane.

The yield of hydrogen, which is not balanced by the extent of unsaturation in the dimers, trimers and tetramers necessitates the assumption that the higher polymers must contain rings or more than one double bond per molecule. A reaction scheme involving scission of a carbon-hydrogen bond in an olefin yielding a hydrogen atom and a radical would be incompatible with the experimental findings. However, the production of hydrogen in the radiolysis of paraffins has been attributed largely to a molecular process.<sup>6,23,24</sup> Molecular production of

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hydrogen from an olefin molecule would result in the formation of a diene which would be very reactive in chain polymerization.

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## Ionization Potentials of Some Olefins, Di-olefins and Branched Paraffins

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The ionization potentials of a number of olefins, cycloolefins, di-olefins and branched paraffins have been measured by electron impact. The results obtained have been compared where possible with ionization potentials obtained by photoionization and by ultraviolet spectroscopy, as well as with earlier electron impact data. Values presented for a number of compounds which had not been investigated previously are consistent with structural considerations. Some inconsistencies in the earlier electron impact data are discussed.

### Introduction

The ionization potentials of a large number of hydrocarbon molecules have been measured by electron impact, and a recent survey<sup>2</sup> shows that for most of these compounds the published data are in satisfactory agreement. For a number of compounds, on the other hand, the existing data show a remarkable spread. For instance, in the values for isobutane and isobutene a spread of nearly 1.0 v. is found among values obtained by different workers. In other cases, as for the pentanes and hexanes, the published ionization potentials do not reflect the structural differences in the manner to be expected. For other branched olefins and for di-olefins very few values are available. The present work represents an attempt to resolve some of the discrepancies and to provide electron impact values for a number of compounds which have not been investigated previously.

### Experimental

The method of obtaining the ionization efficiency curves for the compound and for the added standard gas, usually krypton or xenon, has been described previously.<sup>3</sup>

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**Materials.**—The authors are greatly indebted to Professor K. B. Wiberg and Mr. Jerry Albin of the University of Washington for the gift of a sample of cyclopropene. The other compounds were NBS standard samples or commercial chemicals of high purity.

### Results and Discussion

(a) **Branched Paraffins.**—The values obtained for five branched paraffins are given in Table I, together with the earlier values obtained by electron impact.<sup>4-8</sup> Also included in the table are ionization potentials measured by photoionization<sup>9</sup> and two sets of values calculated using slightly different parameters.<sup>10</sup> It is of interest to note that the values obtained in this work parallel almost exactly the photoionization data, the former being in each case higher by 0.24-0.30 v. Since the transitions brought about by electron impact and by photon impact should both be vertical transitions, this constant difference must arise from a difference in the means of interpreting the ionization threshold in the two methods. By comparison with the earlier electron impact data for isobutane, the present data are in best agree-

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