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RADIOLYSIS OF LIQUID PROPYLENE: ION-MOLECULE CONDENSATION

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Abstract—Radiolysis of propylene gives mainly hydrogen, and dimeric, trimeric, and other low molecular weight polymeric hydrocarbons.

Detailed analysis of the dimer shows the products to be, in order of concentration, 4-methyl-1-pentene, 1,5-hexadiene, 1-hexene, 2-methylpentane, 2,3-dimethylbutane, 4-methyl-2-pentene, 2-methyl-1-pentene, 2-hexene, and n-hexane.

The relative product concentrations, and the isotope species distribution in the products obtained from radiolysis of a 50:50 mixture of propylene and propylene-d_6, demonstrate that the alkanes, the diene, and much of the olefinic products are formed by combinations of n-propyl, isopropyl, and allyl radicals.

Isotopic species distributions in 4-methyl-1-pentene, 1-hexene, and 2-hexene demonstrate that appreciable fractions of each of these products are formed by a direct condensation of two propylene molecules with intramolecular hydrogen rearrangement. The previously postulated direct dimerization is thus verified, and the idea of its being an ion-molecule condensation receives further support.

INTRODUCTION

THE radiolysis of olefins in liquid phase gives mainly low molecular weight monoolefinic polymers, with some hydrogen and some alkane derived from the alkene.[1] Skeletal structures of the dimers are relatively simple; for example, 1-hexene gave dimeric monoolefins with mainly straight chain and 5-methylundecane skeletons. Lack of C_2 or C_3 branching was believed to indicate only a minor role of allyl-type free radicals. Temperature insensitivity of product distribution required that any entities in thermal equilibrium must not be reacting by paths requiring significant activation energy. Therefore, it was postulated that a new and important reaction in liquid phase is the direct addition of a molecule ion to a molecule, with rearrangement of hydrogen atoms and charge neutralization to give the monoolefinic dimer.

Further conclusions from the C_6 system were difficult to obtain because of complexity of product distribution. A study of propylene radiolysis was undertaken because the number of possible dimeric products is smaller. Hence, essentially complete analysis of the dimer was possible. Furthermore, propylene-d_6 was available, so that experiments could be performed to provide information on the role of the hydrogen atoms.

EXPERIMENTAL

Propylene. Phillips Research Grade propylene was distilled at −78° into a 2 cm o.d. Pyrex irradiation ampule, and sealed *in vacuo*. The sample, weighing 16·7 g, was irradiated by bremsstrahlung in a Dewar at −78° just beneath the slanting gold target[2] of a 3 MeV Van de Graaff, using a 1 mA beam and a 1½ in. linear scan. The dose in the two hour irradiation was determined by ceric ion dosimetry, using identical geometry, to be $3{\cdot}48 \times 10^7$ rads.

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[1] P. C. Chang, N. C. Yang and C. D. Wagner, *J. Amer. Chem. Soc.* **81**, 2060 (1959).

[2] C. D. Wagner and V. A. Campanile, *Nucleonics* **17**, [7] 99 (1959).

Volatile products isolated by Toepler pumping at −196° were analyzed mass spectrometrically. Unreacted feed (plus any propane and C_2 material) was collected by distillation at −78° and analyzed similarly. The volatile part of the residue was distilled at 70° into a small tube, sealed, weighed, and later analyzed by gas chromatography. The remaining residue was weighed and analyzed by gas chromatography for presence of C_6 compounds; none was present.

For the gas chromatographic analysis, two different columns were used. With a 40 ft Ucon-filled column at 50°, the spectrum shown in Fig. 1 was obtained. Peaks on this record were identified by a combination of retention-time of known materials and mass spectrometric identification of isolated samples. More accurate quantitative analysis was provided by a 100 m glass capillary column with

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THE FORMATION OF 3(OR 5)-METHYLCYCLOPENT-2-EN-2-OL-1-ONE* FROM ACETONE

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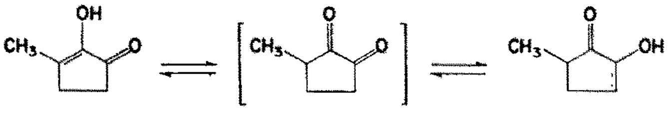
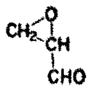
(*Received* 27 *January* 1961)

Abstract—The original observation that 3(or 5)-methylcyclopent-2-en-2-ol-1-one (I) was formed (in low yield) by the treatment of glycidaldehyde with acetone in the presence of aqueous alkali, and speculations concerning the reaction mechanism, led to the realization that the reaction could also be carried out with glyceraldehyde. This suggested an explanation for the previously known formation of I by drastic alkali-treatment of carbohydrates.

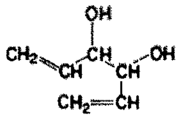
The treatment of glycidaldehyde (II)[3] with acetone and aqueous alkali afforded, in low yield, a crystalline solid of composition $C_6H_8O_2$, which was found to be identical with the known 3(or 5)-methylpent-2-en-2-ol-1-one (I).[1,2] This compound is a minor product of the destructive distillation of wood,[4] and has also been obtained from wood by the action of hot aqueous alkali under pressure.[5] It has previously been synthesized (a) by dehydrogenative cyclization of 3,4-dihydroxyhexa-1,5-diene (III) with copper,[6]



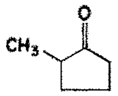
Ib Ia Ic



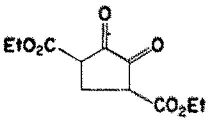
II



III



IV



V

VI

(b) from 2-methylcyclopentanone (IV) by chlorination and subsequent hydrolysis of the resulting dichloro-derivative,[7] (c) from 3,5-diethoxycarbonylcyclopentan-1,2-dione

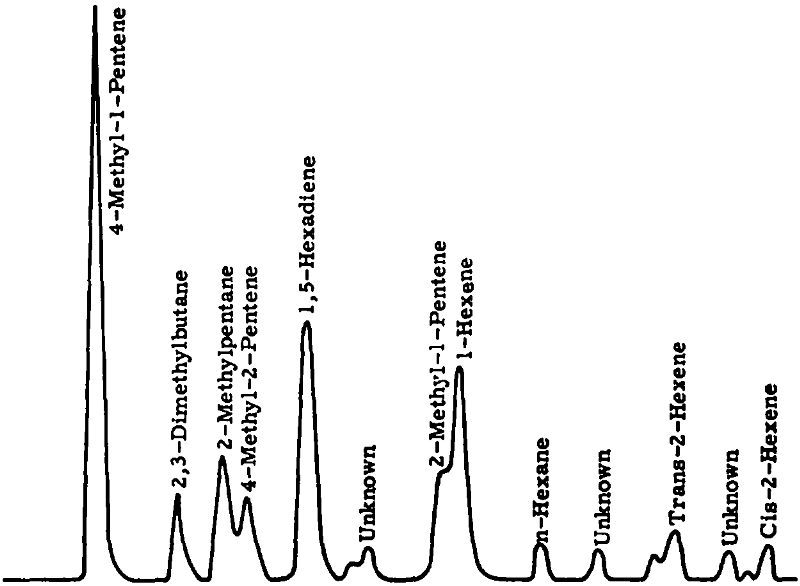


FIG. 2. Analysis of dimer by GLC. 100 m glass capillary column with silicone-filling at 25°.

subtracted. If the compound was known to give negligible fragmentation in the C_n group (for example, with hexene, ions of $m/q = 72$–83 have negligible intensities compared to that of $m/q = 84$), the ion intensities were taken as those of parent ions and as representative of species distribution. If fragmentation is significant, species analysis was performed by subtracting contributions of parent and fragment ions of successively lighter species, with the assumption that there are no significant isotope effects in fragmentation.

RESULTS

Propylene. Yields of products are shown in Table 1. The *G*-value for conversion of propylene to dimer is 2·16, while the *G* for total converision is ca. 9. Most of the minor unknown products in Table 1 (shown in Fig. 1) have retention times longer than n-hexane, and may be 1,4-hexadiene, 2,3-dimethyl-1-butadiene, and/or *cis*- and *trans*-3-hexene.

Propylene plus propylene-d_6. Mass spectrometric information was obtained on the dimer hydrocarbon cuts obtained by gas chromatography, shown in Fig. 1. Isotopic species distributions that were calculable from mass spectra are given in Table 2. Cut 9 was thought to be a mixture of *trans*-2-hexene and 1,5-hexadiene. In the mass spectrum of this cut the ion intensity ratio for $m/q = 95$ to $m/q = 96$ was 0·41; other ions could not be analyzed as originating with either single component, so that other data obtained on this cut were not meaningful. Cut 10 was mainly 1,5-hexadiene, but the large contribution of hydrogen-poor fragment ions in the C_6 portion of the spectrum made isotopic analysis impossible. Cut 11 was an unknown hexadiene with a large parent ion in the C_6 region.

DISCUSSION

Product analysis for isotopic species in a system composed of equal amounts of two such isotopic species provides useful information on reaction mechanism. For example, if isotope effects are neglected, formation of hexene by simple combination of two propylene molecules with no other molecules or molecular fragments participating

TABLE 1. PRODUCTS OF PROPYLENE RADIOLYSIS

	%m	G
Hydrogen	0·26	0·6
Methane	0·02	0·04
Propane[a]	0·1	0·2
butane[b]	0·01	0·02
1-Butene[b]	0·012	0·02
2-Butene[b]	0·012	0·02
Pentene[b]	0·008	0·02
Pentadiene[b]	0·008	0·02
2,3-Dimethylbutane	0·032	0·054
2-Methylpentane	0·048	0·080
n-Hexane	0·0133	0·022
4-Methyl-1-pentene	0·227	0·375
4-Methyl-2-pentene[c]	0·033	0·055
2-Methyl-1-pentene	0·02	0·033
1-Hexene	0·085	0·14
trans-2-Hexene	0·018	0·030
cis-2-Hexene	0·0133	0·022
1,5-Hexadiene	0·104	0·17
Others (6)	0·048	0·08

[a] Analytical scheme gave unreliable results for ethylene, but a small amount was clearly present

[b] Values obtained from analysis of Fig. 1.

[c] Identification not certain, based only on retention time of standard.

TABLE 2. ISOTOPIC SPECIES DISTRIBUTION IN PRODUCTS FROM $C_3H_6 + C_3D_6$. MOLE PER CENT SPECIES IN COMPOUND, BY DEUTERIUM ATOMS PER MOLECULE[a]

Cut	Compound	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
6	2-Methylpentane +2,3-Dimethylbutane	3·2	11·7	11·3	0·5	3·9	0·6	6·6	20·8	18·9	0·6	1·6	0·3	2·7	8·4	8·9
7	4-Methyl-1-pentene			9·5	8·5	1·2	0·8	1·0	8·0	31·8	8·9	1·3	0·5	1·6	7·1	21·2
8	1-Hexene + 2-methyl-1-Pentene			14·8	10·1	1·4	0·3	0·7	6·8	29·8	10·1	1·0	0·4	1·0	5·8	17·7
11	Hexadiene					12·5	3·6	5·8	2·2	5·5	22·6	9·0	9·3	8·1	4·5	17·1

[a] Analysis assuming no isotope effect in parent ion sensitivity or in fragmentation pattern.

would provide hexene-d_{12}: hexene-d_6: hexene-d_0 in the ratio of 1 : 2 : 1, with no other species. Formation of hexene by combination of C_3H_6, CH_3, and C_2H_3 moieties from different molecules would give species hexene-d_{12}: hexene-d_9: hexene-d_6: hexene-d_3: hexene-d_0 in the ratio 1 : 2 : 2 : 2 : 1. Thus, with no isotope effect, a single mechanism would provide a simple species distribution.

The existence of appreciable isotope effect in most reactions involving deuterium and protium compounds is both a complicating factor and a useful factor. It is a complicating factor in that the quantitative relationship is not the simple statistically-derived one. It is a useful factor in that its magnitude can sometimes provide information on the mechanism.

2-*Methylpentane and* 2,3-*dimethylbutane.* Significant parent ion intensities were found for -d_{14}, -d_{13}, -d_{12}, -d_8, -d_7, -d_6, -d_2, -d_1, and -d_0. (The value for -d_{10} is spurious; it is due to pre-emergent hexene-d_{12}.) The mode of formation obviously involves two C_3H_6 entities plus two hydrogen atoms, obtained independently from four molecules.

This would result if the mechanism involves union of two propyl radicals, each derived from C_3H_6 (or C_3D_6) plus H or D (cf. discussion on radical formation below).

Let us assume that these compounds are formed from combinations of propyl and isopropyl radicals present in steady-state concentrations during the irradiation, and determine whether product distribution is consistent with the assumption. With low overall conversion, product distribution reflects initial rates of formation. If we assume all rate constants for combination of these radicals are identical, we can calculate relative steady-state concentrations for each propyl isotopic species: propyl-d_7, propyl-d_6, propyl-d_1, and propyl-d_0 (with no differentiation here between n-propyl and isopropyl).

When this is done from the data for d_{14}, d_{13}, d_{12}, d_8, and d_6, we obtain the following relative steady-state concentrations, normalized to unity:

$$R_7 = 0{\cdot}18$$
$$R_6 = 0{\cdot}34$$
$$R_1 = 0{\cdot}19$$
$$R_0 = 0{\cdot}28$$

and we see the sum $R_7 + R_6$ is close to that of $R_1 + R_0$, indicating nearly equal probabilities of participation by C_3H_6 and C_3D_6 in the formation of propyl. On the other hand, $R_7 = 0{\cdot}54\ R_6$ and $R_1 = 0{\cdot}68\ R_0$. Thus there is a substantial isotope effect favoring H over D for participation in propyl formation. These facts will be used below in a discussion of the mechanism of propyl radical formation.

As a check on the assumption of hexane formation by radical combination, the -d_7, -d_2, -d_1, and -d_0 species destribution calculated from the above relative steady-state radical species concentration is compared with experiment in Table 3.

TABLE 3. BRANCHED HEXANE ISOTOPIC SPECIES DISTRIBUTION

	Found (%)	Calc. (%)
d_7	22·5	23·5
d_2	2·9	3·7
d_1	9·1	10·9
d_0	9·6	8·1

The reasonable agreement between calculated and observed values in Table 3 and the reasonable values for relative steady-state propyl species concentrations provide good evidence that the saturated hydrocarbons are formed by propyl radical combination. It will be shown later that the relative amounts of n-hexane, 2,3-dimethylbutane, and 2-methylpentane among the products are consistent with a particular relative steady-state concentration of n-propyl and isopropyl.

4-Methyl-1-pentene. This compound is the major volatile product. Important amounts of -d_{11}, -d_7, -d_5, and -d_1 species, in addition to the expected -d_{12}, -d_6, and -d_0, indicate a major mode of formation involves union of C_3H_6, C_3H_5, and H moieties from separate molecules. We may assume the major mechanism involves combination of isopropyl and allyl radicals. However, inspection of the data shows that the amounts of -d_{12}, -d_6, and -d_0 species appear disproportionately large. Let us assume there are two mechanisms, the radical combination reaction and a "direct" mechanism, the latter giving the excess amounts of the -d_{12}, -d_6, and -d_0 species. The contributions of each may be calculated from the data. To do this, three isotope effects must be considered in the radical combination reaction. These are the probabilities of appearance in the product of C_3D_6 compared to C_3H_6, C_3D_5 compared to C_3H_5, and D compared to H. From the observed ratio -d_{11}/-d_5, the first, $(C_3D_6)/(C_3H_6)$, is found to be nearly unity, consistent with the finding on propyl radicals in hexane formation. From the observed ratio -d_{11}/-d_7, the second, $(C_3D_5)/(C_3H_5)$ can be expressed in terms of the third, (D)/(H). With the sum of observed mole fractions of -d_{11}, -d_7, -d_5, and -d_1 species as a basis, distributions of all species formed by radical combination can then be calculated for any assumed value of (D)/(H). The value of (D)/(H) for propyl radicals in generating the branched hexanes was found to be 0·54–0·68. If 0·6 is used, one obtains the distribution shown in Table 4. For this purpose the small apparent contribution (6 per cent) of other species are ignored. Subtraction of the calculated distribution from the observed distribution gives the excess amounts of -d_{12}, -d_6, and -d_0 species formed by the direct reaction, shown in Table 4. Note that the value for -d_6 is reasonable, in the sense that it is close to twice the geometric mean of -d_0 and -d_{12}. Approximately 28 per cent of the product is formed by the direct reaction. This value is quite insensitive to values assumed for (D)/(H); it varies only from 24 to 31 per cent for values of (D)/(H) between 0·5 and 0·8. Inclusion of the second order correction for the fact that the feed C_3D_6 is 3·5 per cent C_3D_5H has a negligible effect on the results, but accounts for some of the -d_4 and -d_{10} species observed.

TABLE 4. SPECIES DISTRIBUTIONS IN 4-METHYL-1-PENTENE

	Obs. (%m)	Radical reaction calc. (%m)	Direct reaction (%m)
-d_{12}	10·0	5·3	4·7
-d_{11}	8·9	8·8	
-d_7	8·4	8·3	
-d_6	33·4	19·0	14·4
-d_5	9·35	8·8	
-d_1	7·45	8·3	
-d_0	22·2	13·8	8·5
			27·6

1-*Hexene* + 2-*Methyl*-1-*pentene.* A similar treatment can be applied to the data on this fraction, yielding the following information;

(1) The fact that -d_{11}/-d_5 is unity indicates again that the probability ratio for $(C_3D_6)/(C_3H_6)$ entering into the radical reaction is unity.

(2) The value for (D)/(H) ratio for the radical reaction appears to be in the range 0·5–0·8.

(3) Approximatley 28–32 per cent of the combined product appears to arise from the "direct" reaction. (A major fraction of this may well be the 2-methyl-1-pentene, since the latter is probably not formed by combination of radicals.)

It is concluded the radical reaction to form 1-hexene probably involves the combination of n-propyl and allyl radicals.

1,5-*Hexadiene.* This compound is undoubtedly formed by allyl radical combination. As mentioned above, the isotopic species distribution could not be determined to verify this point.

2-*Hexene.* The ion intensity ratio 95/96 of only 0·41, compared to 0·89 for 4-methyl-1-pentene, demonstrates that a major fraction of the 2-hexene is formed by a direct mechanism.

Unknown hexadiene. The mass spectrum of this compound has low fragment ion intensity in the C_6 region. 2,3-Dimethyl-1,3-butadiene and 2-methyl-1,3-pentadiene, both possibilities on the basis of boiling point, have 81/82 ion intensity ratios of 0·17 and 0·25 respectively.[3] A significant amount of d_9 species ($d_9/d_{10} = 0{\cdot}29$) requires that the reaction be no more than 60 per cent simple recombination of C_3H_5 radicals. Since at least one of the radicals would have to be crotyl or $CH_3—\underset{\cdot}{C}=CH_2$, rather than allyl, it is not surprising that the product is not entirely formed by abstraction of hydrogen from propylene followed by simple radical combination.

ROLE OF FREE RADICALS

The isotopic species distribution for individual compounds has been examined above to obtain information on the mechanism of formation. The relative amounts of the compounds themselves should also furnish some information. If we assume that steady-state concentrations of n-C_3H_7, i-C_3H_7, and C_3H_5 (allyl) radicals exist during the radiolysis, we can determine the consistency of the distribution of the products formed by combination. If we assume for the moment that this is the only mechanism and that the collision efficiencies of the radical combination reactions are equal, we obtain from the relative concentrations of n-hexane, 2,3-dimethyl butane, and 1,5-hexadiene the following relative steady-state concentrations of free radicals: n-propyl, 0·18; isopropyl, 0·29; and allyl, 0·52. Calculation from these gives the amounts of cross-products shown in Table 5. In this table, observed product concentrations are normalized to 100 per cent. The value for 2-methylpentane is not far from the calculated value, and this strengthens the previous conclusion that the alkanes are formed by propyl radical recombination. The calculated values for 4-methyl-1-pentene and 1-hexene are 52 per cent and 87 per cent of those observed, respectively, whereas isotopic species distribution would indicate the contribution by this free

TABLE 5. OBSERVED AND CALCULATED DISTRIBUTIONS OF MAJOR PRODUCTS

	Obs.	Calc
n-Hexane	2·6	
2,3-Dimethylbutane	6·4	
1,5-Hexadiene	20·4	
2-Methylpentane	9·4	8·1
1-Hexene	16·7	14·5
4-Methyl-1-pentene	44·5	23

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[3] API Project 44 Mass Spectra.

radical mechanism should be 69–76 per cent for 4-methyl-1-pentene and ca. 85 per cent for 1-hexene.

It is of interest to note that the sum of the n-propyl and isopropyl concentrations is calculated to be almost equal to that of allyl. Two mechanisms of formation of the radicals come to mind that have this stoichiometry and involve no activation energy restrictions:

$$C_3H_6^+ + C_3H_6 \rightarrow C_3H_7^+ + C_3H_5\cdot \qquad (1)$$

$$C_3H_7^+ + \epsilon \rightarrow C_3H_7^*\cdot$$

$$C_3H_6^* \rightarrow C_3H_5\cdot + H \qquad (2)$$

$$H + C_3H_6 \rightarrow C_3H_7\cdot$$

Reaction (1) is an ion-molecule reaction first observed by Tal'roze and Lyubimova[4] in a mass spectrometer, and shown by Schissler and Stevenson[5] to have a very high cross-section. The propyl ion, on neutralization, should give propyl radical; ordinarily, isopropyl would be expected to be the favored product, but the necessity for passage through energy-rich periods on reaction and electron recombination might lead one to expect both isomeric radicals. In reaction sequence (2) on the other hand studies have shown that hydrogen atom addition proceeds almost exclusively to the terminal carbon at either 25°[6] or −196°.[7] Formation of n-propyl radicals therefore cannot be accounted for by this path.

It is still necessary to account for the isotope effect in propyl formation. There is an isotope effect in participation of H or D, but not of C_3H_6. Whether the magnitude of the effects can be explained by differences in cross-sections for the ion-molecule reaction in liquid phase is not known.

NATURE OF THE "DIRECT" DIMERIZATION

Regarding direct dimerization we have the following facts:

(1) About 30 per cent of the dimer olefin from propylene is formed by a mechanism involving only the hydrogen atoms of the reacting molecules.

(2) Most of the dimer olefin molecules from 1-hexene[1] have carbon skeletons of n-dodecane or 5-methylundecane.

On the basis of (2), an ion molecule mechanism was proposed,[1] in which an electron-deficient olefin molecule, or molecule-ion, reacts with the double bonded end of a neighboring uncharged molecule. This, followed by intramolecular hydride transfer and electron recombination gives dimer olefin;

$$C_nH_{2n}^+ + C_nH_{2n} \rightarrow [C_{2n}H_{4n}]^{\div} \xrightarrow[\text{transfer}]{H^-} C_{2n}H_{4n}^+ \overset{\epsilon-}{\rightarrow} C_{2n}H_{4n}^* \rightarrow C_{2n}H_{4n}$$

The confirmation with labeled propylene of the intramolecular nature of the reaction with respect to hydrogen atoms provides further support for the mechanism.

Indirect evidence for the condensation step includes:

(1) Pottie and Hamill[8] have observed dimeric ions from alkyl iodides with lifetimes greater than a microsecond, by ionization in a mass spectrometer.

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[4] V. L. Tal'roze and A. K. Lyubimova, *Dokl. Akad. Nauk SSSR* **86**, 909 (1952).

[5] D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.* **24**, 926 (1956).

[6] W. L. Moore, *J. Chem. Phys.* **16**, 916 (1948).

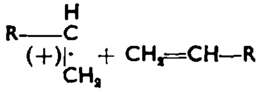
[7] R. Klein and M. D. Scheer, *J. Phys. Chem.* **62**, 1011 (1958).

[8] R. F. Pottie and W. H. Hamill, *J. Phys. Chem.* **63**, 877 (1959).

(2) Barker[9] with similar techniques observed dimeric ions from benzene, up to $C_{12}H_{11}^+$.

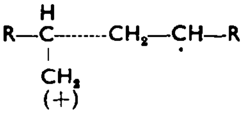
(3) Field, Franklin and Lampe[10] pointed out that heavier ionic products from ion-molecule reactions of ethylene in the mass spectrometer are similar in relative yield to the relative abundances of the same ionic products in the fragmentation of the corresponding C_4 compounds under electron impact in the mass spectrometer. The similarity indicates an unstable dimeric ion was an intermediate in the ion-molecule reaction.

The data on dimeric products of 1-hexene[1] indicate condensation occurs at the double bonded carbons of the two molecules. In that discussion it was pointed out that the excess electron density in the normal olefin molecule is about 0·1 on the terminal double-bonded carbon, with the electron deficiency distributed over the neighboring carbons. On the other hand, in the molecule ion the electron deficiency is shared nearly equally by the two double-bonded carbons. Thus, it may be expected that the attack is the following:



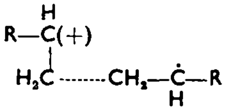
$$\mathrm{R{-}\overset{H}{C}\underset{CH_3}{\overset{(+)|\cdot}{}} + CH_2{=}CH{-}R}$$

to give either:



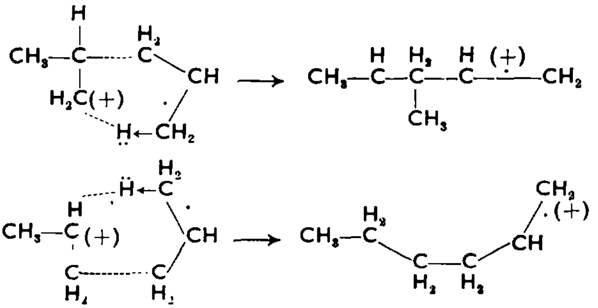
$$\mathrm{R{-}\overset{H}{\underset{\underset{(+)}{CH_3}}{C}}\cdots CH_2{-}\underset{\cdot}{CH}{-}R}$$

or



$$\mathrm{R{-}\overset{H}{C}(+){-}H_2C\cdots CH_2{-}\underset{H}{\dot{C}}{-}R}$$

In the case of propylene, hydride transfer in a ring transition state would give the proper product configuration, requiring only charge neutralization and dissipation of the acquired ionization energy to give the major monoolefin products:



Hydride transfers are common in carbonium ion chemistry and have also been observed in gaseous, unsolvated systems.[11]

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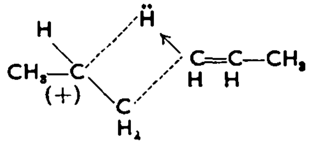
[9] R. Barker, *Chem. & Ind.* 233 (1960).

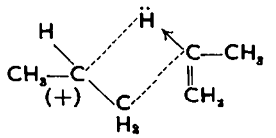
[10] F. H. Field, J. L. Franklin and F. W. Lampe, *J. Amer. Chem. Soc.* 79, 2665 (1957).

[11] F. H. Field and F. W. Lampe, *J. Amer. Chem. Soc.* **80**, 5587 (1958).

Indications were that 2-hexene was formed from propylene predominantly by this direct mechanism. In this instance a smaller ring or the equivalent would be required:

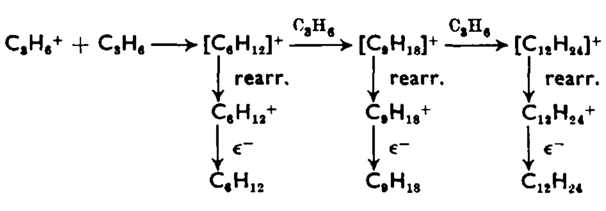


2-Methyl-1-pentene was a minor product. It was isolated only with a much larger amount of 1-hexene. It seems probable it could be formed by the similar direct mechanism, with attack at the central carbon:



In the condensation step and particularly at the electron recombination step, a problem of energy dissipation exists. The overall sequence from the ion and molecule is exothermic by 10·5 eV, with about 1 eV acquired in the condensation step and 9·5 eV contributed by the ionization energy in the neutralization step. It is believed that fragmentation of these excited species is prevented by the proximity of the neighboring molecules. During the existence of the ion the positive charge induces polarization in the immediately adjacent molecules, and the electrostatic energy of the system is thus diffused over several molecules. Energy transfer can occur not only by vibrational energy transfer in collisions, but also by electrostatic interactions. Thus, as the ion is neutralized, the ionization energy is acquired by the whole cluster as depolarization occurs. Since the energy stored in the surrounding cluster is proportional to r^{-4}, calculation of the contribution by the clustering molecules is extremely sensitive to the value assumed for r. However, for distances of the order of Angstroms, energy storage can be an appreciable fraction of the 9·5 eV.

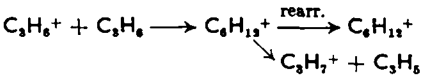
The proposed mechanism allows possible further polymerization before electron recombination:



$$\begin{tikzcd} C_3H_6^+ + C_3H_6 \arrow[r] & {[C_6H_{12}]^+} \arrow[r, "C_3H_6"] \arrow[d, "\text{rearr.}"] & {[C_9H_{18}]^+} \arrow[r, "C_3H_6"] \arrow[d, "\text{rearr.}"] & {[C_{12}H_{24}]^+} \arrow[d, "\text{rearr.}"] \\ & C_6H_{12}^+ \arrow[d, "\epsilon^-"] & C_9H_{18}^+ \arrow[d, "\epsilon^-"] & C_{12}H_{24}^+ \arrow[d, "\epsilon^-"] \\ & C_6H_{12} & C_9H_{18} & C_{12}H_{24} \end{tikzcd}$$

Dimerization would thus represent the special case where the chain is terminated by neutralization at that stage.

On first sight it might seem that the formation of propyl ions and allyl radicals should represent an alternative reaction path for the hexene ion complex:



$$\begin{tikzcd} C_3H_6^+ + C_3H_6 \arrow[r] & C_6H_{12}^+ \arrow[r, "\text{rearr.}"] \arrow[dr] & C_6H_{12}^+ \\ & & C_3H_7^+ + C_3H_5. \end{tikzcd}$$

However, the $C_3H_7^+$ is formed very specifically from a propylene ion plus one hydrogen from another molecule, while one should expect such a decomposition to provide at least some further mixing of hydrogens. That specific atom transfers can occur without mixing in ion-molecule reactions where product ions are of weight intermediate between primary and dimer ion is shown in the reaction $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$.[12] Therefore, it is believed that these reactions result from a dimeric ion complex of higher energy and shorter life-time, a complex formed from a propylene ion possessing excess vibrational energy acquired in the primary ionization act.

A mechanism alternative to the ion-molecule condensation, yet consistent with intramolecular role of the hydrogen, is the concept that propyl and allyl radicals formed in this way recombine before they leave the reaction cage. This mechanism cannot explain the specificity of carbon skeletons in the dimer from 1-hexene, nor can it be extended to account for the higher molecular weight polymers.

Another possible mechanism is similar to that invoked by Dole, Milner and Williams,[13] involving reaction of double-bonded carbons in an activated state with a neighboring saturated chain. Such a mechanism applied to these olefinic systems would have to represent a special case of attack at the double bond, rather than an alkyl chain. A mechanism involving excited molecules cannot be rejected, but on the other hand, there is no supporting evidence for its occurrence in this system.

This system with propylene in a sense represents a special case of olefin radiolysis, for propylene is a small molecule and its derivative, the allyl radical, is symmetrical. The fact that the fraction of monoolefin in the dimer is only 0·64, compared to ca. 0·9 with 1-hexene, indicates that the direct dimerization is more important with larger olefins. The greater number of modes of energy dissipation in large molecules may be responsible for the difference. A central feature of the ion-molecule mechanism for condensation is the necessity that close neighboring molecules participate in electrostatic and collisional energy transfer. For this reason these condensations are probably peculiar to liquid or solid phase.

CONCLUSIONS

(1) An important amount of dimeric product is formed by a direct condensation of two olefin molecules, believed to proceed as an ion-molecule condensation, followed by hydrogen atom rearrangement and charge neutralization.

(2) With propylene the saturated hexanes (2,3-dimethylbutane, 2-methylpentane, and n-hexane) are formed by combination of n-propyl and isopropyl radicals. Much of the olefinic dimer not formed by direct ion-molecule condensation is formed by combination of allyl with propyl or isopropyl radicals.

(3) Formation of propyl radicals involves addition of atoms of hydrogen to propylene, by a mechanism that gives a significant fraction (38 per cent) of n-propyl. This lack of specificity is evidence against addition of thermal hydrogen atoms to propylene, so an ion-molecule mechanism is proposed.

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[12] C. D. Wagner, P. A. Wadsworth and D. P. Stevenson, *J. Chem. Phys.* **28**, 517 (1958).

[13] Malcolm Dole, D. C. Milner and T. F. Williams, *J. Amer. Chem. Soc.* **80**, 1580 (1956).