

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Thermal Rearrangements among the Pentenes

BY CHARLES D. HURD, GEORGE H. GOODYEAR AND A. R. GOLDSBY

2-Pentene has been studied previously by Norris and Reuter.¹ They found it to be two-thirds decomposed in fourteen seconds at 600°. The moles of gaseous products found were: CH₄ 100, C₄H₆ 30, C₄H₈ 27, C₃H₆ 21, C₂H₄ 15. There was no hydrogen or ethane. The study was not designed to include the identification of the various butylenes or pentylenes. Pease and Morton² who studied the kinetics of the pyrolysis of 2-pentene, found it to be a pseudo-unimolecular, homogeneous gas reaction. 2-Pentene has also been pyrolyzed in metal tubes.³

In the present study at 500–600°, both 1-pentene and 2-pentene were included. For completeness, the entire gaseous reaction product was analyzed but especial attention was devoted to the C₄ and C₃ components of the mixture. It was found that 2-pentene possessed somewhat greater stability than 1-pentene. Over half of the reaction products from both were gaseous. Methane, 1-butene, propylene, ethane and ethylene in molar quantities respectively of 6:2:2:2:1 accounted for over nine-tenths of the gas. Small quantities of 2-butene, butadiene and hydrogen were formed also. Some propane was produced from 1-pentene but not from 2-pentene. Regardless of the pentene taken, about six moles of 1-butene appeared for each mole of 2-butene.

The isomerization of 1-pentene (b. p. 30°) into 2-pentene (36°) and *vice versa* at temperatures above 580° was established by precise distillation. The requirement of such high temperatures for this rearrangement is significant and parallels the high temperature which was found necessary to induce isomerization in the butenes.⁴ The non-formation of isopropylethylene from pure 2-pentene is evidence against an allylic type of intramolecular wandering of the methyl radical. By analogy, this also excludes intramolecular wandering of the hydrogen radical as the mechanism for the conversion of 1- or 2-pentene into each other, especially since more energy is required to break aliphatic C–H bonds than C–C bonds. The fact that temperatures of about 600° are required to

initiate the rearrangement of 1- into 2-pentene suggests that the rearrangement is subject to the same type of mechanism as that which accounts for the production of smaller hydrocarbon products.

The liquid products boiling above 60° consisted both of aromatics and of unsaturates. On the basis of Wheeler and Wood's⁵ work on the butenes, cycloalkenes probably predominated in the latter.

Experimental Part

Synthesis of 1-Pentene.—Kirrmann's method⁶ was used, with modifications. Pure ethyl bromide (136 g.) was added dropwise to a mixture of 32 g. of magnesium and 425 cc. of butyl ether.⁷ When reaction was complete the mixture was filtered rapidly through glass wool. This solution was dropped during three hours into 84 cc. of pure allyl bromide and 340 cc. of butyl ether. The flask was then connected to a 60-cm. Davis column⁸ and the pentene distilled off directly by using an oil-bath, eventually heated to 140°. Redistillation through the column gave 2 cc. of isopropylethylene,⁹ collected at 21–23°, and 38 g. (54% yield) of 1-pentene, b. p. 29–31°, *n*_D²⁰ 1.3717 (Kirrmann reported 1.3714 for pure 1-pentene). This material was used in the three runs listed in Table I.

The index of refraction proved to be an unreliable criterion of purity, for isopropylethylene persisted in this fraction. A second redistillation through the Davis column gave a small fraction at 20° as before. The 29–31° fraction, on a third distillation, gave no low-boiling material. Practically the entire amount distilled (754 mm.) at 29.1–30.0°.

Other Modifications Tried.—The yields obtained when allyl bromide was dropped into the ethylmagnesium bromide were much poorer, namely, 25 and 9% in experiments conducted, respectively, at 20 and 70°. Side reactions predominated in the 70°-run to form considerable diallyl and much gas (44% paraffins, 34% ethylene, 22% other olefins).

2-Pentene (First Method).—Technical 2-pentanol was dehydrated in the usual way¹⁰ with 60% sulfuric acid. The material was carefully fractionated in the Davis col-

(5) Wheeler and Wood, *J. Chem. Soc.*, 1819 (1930).

(6) Kirrmann, *Bull. soc. chim.*, **39**, 988 (1925).

(7) The butyl ether was furnished through the courtesy of the Commercial Solvents Corporation, Terre Haute, Ind. Kirrmann used propyl ether.

(8) Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

(9) This unlooked-for contaminant has been observed also by Sherrill, Mayer and Walter, *This Journal*, **56**, 927 (1934). No mention of it was made, however, by Dykstra, Lewis and Boord, *ibid.*, **52**, 3402 (1930), but they did report small amounts of isopentane.

It was the incompletely removed isopropylethylene that occasioned the erroneous statement in *Ind. Eng. Chem.*, **26**, 50 (1934), that isopropylethylene was formed from 1-pentene. That from 2-pentene was likewise traced to a preexisting impurity.

(10) "Organic Syntheses," Coll. Vol. I, p. 421.

(1) Norris and Reuter, *This Journal*, **49**, 2626, 2639 (1927).

(2) Pease and Morton, *ibid.*, **55**, 3196 (1933).

(3) Hurd and Eilers, *Ind. Eng. Chem.*, **26**, 776 (1934).

(4) Hurd and Goldsby, *This Journal*, **56**, 1812 (1934).

TABLE I
 PYROLYSIS OF THE PENTENES

	1-Pentene			2-Pentene		
	550	580	600	550	580	600
Temperature, °C.	550	580	600	550	580	600
Contact time, sec.	8	18	13	12	13	19
Decomposition, %	20	56	58	5	23	54
Pentene taken, g.	46	52	65.4	132	146	97
1-Pentene recovered, g.	37	23	27.5
2-Pentene recovered, g.	125	113	45
Duration, min.	63	167	162	245	321	357
Vol. (S. T. P.) of exit gas, l.	1.38	6.43	11.22	1.41	8.095	16.49
Liquid condensate, g.	41	35	38	129.5	122	70

Analysis of exit gas, per cent. by volume

Propylene		14.7 ^a	17.1 ^a		10.1	10.7
1-Butene		16.0	16.3		13.3	9.8
2-Butene (low-boiling)	} 26.6	1.4	1.7	} 6.2	1.5	} 3.0
2-Butene (high-boiling)		1.1	1.0		0.7	
Butadiene		1.1	1.3		1.5	1.6
Ethylene	12.0	9.1	9.6	6.0	6.2	6.5
Hydrogen	0.0	0.9	1.6	4.2	3.6	5.1
Methane		42.3	35.2	66.9	46.5	50.6
Ethane	} 60.7	12.0	14.7	16.7	15.5	12.7
Propane		1.2	1.3	x	0.8	x
Butane		0.2	0.2	x	0.3	x

^a Includes a small amount of isobutylene.

umn twice. The refractive index (20°) of the 35.8–36.0° fraction (746 mm.), 1.3795, was practically the same as Sherrill's¹¹ (1.3796) for pure 2-pentene. Hence, it was considered sufficiently pure for the study of the gaseous pyrolytic products. This material could not be used, however, in the search for isomeric, branched-chain pentylenes since

Second Method.—3-Pentanol was prepared from ethylmagnesium bromide and ethyl formate as described by Sherrill.¹² It boiled at 114.6–115.6° (758 mm.). Dehydration to 2-pentene was by sulfuric acid.¹⁰ The olefin boiled completely at 35.9–36.1° (745 mm.); n_D^{15} 1.3815.

Apparatus and Procedure.—The set-up of the furnace and connections was similar to that described for the butenes.⁴ There were these modifications. The liquid pentene was forced by mercury displacement into the top of the reaction tube (hot volume, 100 cc.) which was tilted somewhat from the vertical. The effluent gases passed from the 0° trap to a –80° trap, then to a gas receiver. The liquids which were condensed in the traps were distilled through a Davis column to ensure complete removal of the butenes.

The gases were analyzed by liquefaction and distillation¹³ followed by the usual absorption-combustion analysis. The C₄-fraction was analyzed on the Frey-Hepp column as outlined in the paper on the butenes. Three of the distillation curves obtained with this column are shown in Fig. 1. Reference to it will show that the curves are marked into four distillation zones which portray in ascending temperatures: 1-butene, butadiene, low-boiling 2-butene (and also *n*-butane), high-boiling 2-butene. The value for butadiene was confirmed in each case by determining it independently as butadiene tetrabromide. The data are given in Table I.

The liquid products of the various runs were carefully fractionated through the Davis column for the fractions containing the 1-pentene and 2-pentene. As explained above, there was also some lower-boiling isopropylethylene which was discarded. Results for the 600° runs only will be listed, the other runs being comparable.

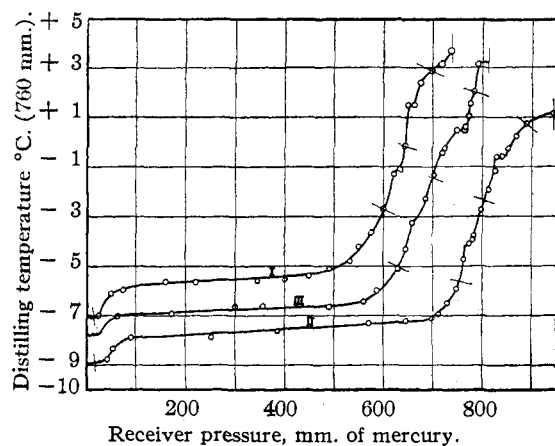


Fig. 1.—Distillation curves of C₄-hydrocarbons. Corrections for ordinates: I, –1°; II, +1°; III, 0°. I. C₄-fraction from pyrolysis of 1-pentene at 580°, 18 seconds. II. From 1-pentene at 600°, 13 seconds. III. From 2-pentene at 580°, 13 seconds.

traces of trimethylene, unremovable by distillation, would vitiate the results. Actually, traces of it were present for a little isopropylethylene appeared to be formed. The synthetic 2-pentene (below) was free from any C₅H₁₀-isomers.

(11) Sherrill, Otto and Pickett, *THIS JOURNAL*, **51**, 3030, 3038 (1929).

(12) Sherrill and co-workers, *ibid.*, **51**, 3026, 3029 (1929).

(13) Hurd, Parrish and Pilgrim, *ibid.*, **55**, 5018 (1933).

From 1-pentene: b. p., cc.: 27-34 (most at 29-32, which is 1-pentene), 27.5; 34-37 which is 2-pentene, 1.5; residue, 3.0.

From 2-pentene: 27-34, 2.9; 34-37, 45; residue 11.5.

The precision of this distillation method makes it evident that rearrangement of 1- to 2-pentene and *vice versa* has occurred.

The residues from the six runs were combined and fractionated: (b. p., cc.) 77-85, 1.0; 85-105, 1.0; 105-115, 1.5; 115-130, 2.0; 130-150, 3.0; residue, 2.0. The refractive index of the 77-85° fraction was 1.448, which is too low for benzene (1.501); yet, sufficient benzene was present to make a satisfactory derivative of *m*-dinitrobenzene. Cyclohexene was probably the other product. The fraction was definitely unsaturated toward bromine in carbon tetrachloride solution. The 105-115° fraction was unsaturated similarly, n_D^{20} 1.4670. The low refractive index was evidence for the presence of a mixture of methylcyclohexene and toluene. Actually, a dinitrotoluene derivative could not be obtained, which pointed to the low concentration of toluene if any.

Liquid Products from the Pure Synthetic Pentenes.—

The synthetic 1-pentene, which had been carefully freed of isopropylethylene, and the synthetic 2-pentene were both subjected to pyrolysis at 550 and 580° with contact times of eight to twenty-two seconds. The same apparatus was used as before. The amount of hydrocarbon taken for each of four runs was 30-39 g. Only the liquid product of these runs was studied. The condensed material was distilled through the Davis column and a reflux ratio of at least 20:1 was maintained. The adapter between the condenser and the receiving bulb was kept ice cold. The tip of the adapter was drawn out to long, capillary dimensions so that it could pass into the slightly larger, long, capillary neck of the tared receiving bulbs, which were also

kept at 0° to avoid possible evaporation losses. The fractionation data from one run each of the two pentenes will be cited.

From 1-pentene: (b. p., g.): 0-18 (dissolved butenes) 1.1; 18-26, 0.03; 26-29.8, 0.14; 29.8-32 (1-pentene), 18.4; 32-34, 1.20; 34-36, 0.92; residue, 2.20.

From 2-pentene: (b. p., g.): 10-18, 0.13; 18-26, 0.13; 26-34, 0.94; 34-36.5, 21.4; residue, 1.5.

No constant boiling portion appeared at 18-26° in either case, indicating an absence of isopropylethylene. The few drops which accrued represented merely the distillation lag. A definite distillation plateau was noticed, however, for 2-pentene from 1-pentene, and for 1-pentene from 2-pentene. Distillation of the combined residues from the 2-pentene runs revealed a sharp rise to 80° and a definite plateau at 82-84°, indicative of cyclohexene; and another at 97-101°, indicative of methylcyclohexene.

Summary

1-Pentene undergoes pyrolytic rearrangement to a small extent into 2-pentene and *vice versa*. This is a high temperature process, occurring at temperatures above 580°. No branched chain isomers are formed from pure 1-pentene or pure 2-pentene. Methane, 1-butene, propylene, ethane and ethylene in molar quantities respectively of 6:2:2:2:1 accounted for over nine-tenths of the gas. Some 2-butene, butadiene and hydrogen were identified also. Evidence was obtained for both aromatics and unsaturates (presumably cycloalkenes) in the liquid products.

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Densities and Refractive Indices of Bromoform-Benzene Mixtures¹

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Mixtures of bromoform and benzene, because of their wide variation in density, have been used for the separation of minerals of different specific gravities.² To facilitate such use we have now determined the densities and indices of refraction of these mixtures over the entire composition range.³

The benzene and bromoform were redistilled, the latter *in vacuo*, until fractions were obtained

(1) Abstract of a thesis submitted by LeRoy Clardy in partial fulfillment of the requirements for the degree of Master of Science in the Graduate School of Texas Christian University.

(2) Sullivan, "Heavy Liquids for Mineralogical Analyses," Dept. of Commerce, Bureau of Mines, Tech. Paper 381, 1927.

(3) But one reference to density data for this system could be found: "I. C. T.," Vol. III, p. 146, with no values given, and the notation that "the reliable data cover less than three values." Öholm, *Medd. Vetenskapsakad. Nobelinst.*, 2, No. 26, 1913.

with a density of 0.8679 for benzene, and an index of refraction of 1.5911 for the bromoform, at 30°. The best values in the literature are respectively, 0.8681 and 1.5980 (at 19°).⁴

The densities were measured with a pycnometer of 2.5 ml. capacity, using a thermostat maintained at 30 ± 0.005°. All values are the mean of six independent measurements with a maximum deviation of 0.00057 and average deviation of 0.00014. The estimated accuracy is 0.02%. The mixtures were made up by weight and were always used within five hours of the time of preparation.

The measurements of the index of refraction were made at 30 ± 0.1° using an Abbe-Spencer

(4) "I. C. T.," Vol. III, p. 29, and Vol. VII, p. 34.