

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE ISOMERS IN "DIISOBUTYLENE." I

BY FRANK C. WHITMORE AND S. N. WRENN

RECEIVED JUNE 3, 1931

PUBLISHED AUGUST 5, 1931

The material known as diisobutylene was first reported by Butlerow.¹ It was prepared by him from isobutylene and sulfuric acid in a sealed tube and by heating tertiary butyl alcohol with dilute sulfuric acid. Similar methods of preparation have since been used by other workers.² Similar materials have been prepared by heating tertiary butyl alcohol with quinoline hydrochloride for three days at 160°;³ by the action of ferric chloride on isobutyl alcohol at 200° for 24 hours;⁴ by heating tertiary butyl iodide with metallic oxides in a sealed tube;⁵ by the reaction of tertiary butyl chloride and isobutylene in the presence of zinc chloride at room temperature;⁶ by the action of zinc chloride on isobutyl alcohol in the presence of hydrogen chloride or traces of isobutyl chloride;⁷ and by the polymerization of isobutylene at high temperature and pressure or in the presence of catalysts.^{2b,8}

It was early recognized that diisobutylene probably consisted of the two isomeric octylenes, 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2. Oxidation experiments indicated the presence of these olefins in varying amounts according to the results of different investigators.⁹ It was not until the work of McCubbin and Adkins that the actual presence of these olefins and their relative proportions were clearly determined.^{2c} They showed that there is about four times as much 2,4,4-trimethylpentene-1 as of its pentene-2 isomer in diisobutylene as prepared by heating tertiary butyl alcohol with approximately 50% sulfuric acid.

The literature contains little information on the physical properties of diisobutylene. The boiling point is given over ranges between 101 and 113° with the most generally accepted values near 103°. The density at 20° is given from 0.715 to 0.7195. Only one reference to the refractive index is given, n_D^{20} 1.41123.^{2b} The melting point is given as

¹ Butlerow, *Ann.*, **189**, 44, 46 (1877).

² (a) Edgar, *Ind. Eng. Chem.*, **19**, 146 (1927); (b) Lebedew and Kobliansky, *Ber.*, **63**, 103 (1930); (c) McCubbin and Adkins, *THIS JOURNAL*, **52**, 2547 (1930).

³ Van Hove, *Bull. Acad. Roy. Soc. Belg.*, 540 (1908); *Chem. Zentr.*, **II**, 292 (1908).

⁴ Oddo, *Gazz. chim. ital.*, **31**, I, 326 (1901).

⁵ Lermontoff, *Ann.*, **196**, 116 (1879).

⁶ Kondakow, *J. prakt. Chem.*, (2) **54**, 442 (1896).

⁷ Malbot and Gentil, *Compt. rend.*, **108**, 957 (1889); *Ann. chim. phys.*, (6) **19**, 370 (1890).

⁸ Ipatiew, *J. Russ. Phys.-Chem. Soc.*, **43**, 1420 (1911); *Ber.*, **44**, 2978 (1911).

⁹ Butlerow, *J. Russ. Phys.-Chem. Soc.*, **14**, 201 (1882); Prileshajew, *ibid.*, **39**, 769 (1907); Wagner, "Dissertation," Warschau, 1888; *Ber.*, **21**, 1230 (1888).

-101°.¹⁰ The present investigation grew out of attempts to make addition products of "diisobutylene." It was soon found that the mixtures obtained were unsatisfactory for study. Many unsuccessful attempts were made to synthesize the individual isomers said to be contained in diisobutylene. It was then decided to attempt the separation of diisobutylene into its isomers by careful fractional distillation. This method proved to be fully as difficult as the results of earlier workers would indicate but has been carried to the point where there is no longer any doubt of its possibility. The results to date are being published because this phase of the work has been interrupted by the departure of one of the authors. The separation is being continued with the use of even more efficient columns than those used in the present study.

A total amount of 19 liters of diisobutylene was subjected to 29 careful fractional distillations during 291 hours of actual distillation.

The purest samples of each isomer obtained have the following properties.

	Boiling point (corr.), Cottrell apparatus, °C.	d_4^{20}	n_D^{20}
Lower isomer	100.1-100.2 (736 mm.)	0.710	1.408
	101.2-101.3 (760 mm.)		
Higher isomer	103.0-103.4 (736 mm.)	0.715	1.415
	104.1-104.5 (760 mm.)		

Since the lower isomer is found in much larger amounts than the higher one and in view of the results of McCubbin and Adkins,^{2b} there can be little doubt that the lower isomer is 2,4,4-trimethylpentene-1 and that the higher isomer is 2,4,4-trimethylpentene-2.

Special experiments showed that diisobutylene does not polymerize or depolymerize on standing in glass bottles exposed to light for over a year or on refluxing at atmospheric pressure for six hours.

In order to make sure that the different properties of the "higher isomer" were not due to impurities of triisobutylene,⁷ a 1:1 mixture of the lower isomer and triisobutylene was fractionated by means of column "H" (see below). No difficulty was experienced in separating the two substances in a single distillation. Since the column used was distinctly inferior to the two columns used in the fractionations of the two isomeric diisobutylenes, the properties of the higher isomer cannot be ascribed to impurities of triisobutylene not removed during the distillations.

Experimental

Preparation of Diisobutylene.¹¹—Individual runs were made in 12-liter flasks provided with reflux condensers. To a cold mixture of 3300 cc. of water and 2700 cc. of c. p. sulfuric acid was added 2500 g. of commercial tertiary butyl alcohol. The thor-

¹⁰ Parks and Huffman, private communication.

¹¹ Based on directions supplied by W. W. Hartman of the Eastman Kodak Company.

oughly shaken mixture was heated on the steam-bath for twenty to thirty hours. Shortly after the heating started an oil began to separate on the surface. The oily layer was removed, washed with water and dilute potassium carbonate solution, dried over calcium chloride for several days and finally refluxed over metallic sodium for five hours. At the end of this treatment fresh sodium retained its metallic luster even after heating in the mixture for an hour. The usual yield was 2100 cc. This, on fractionation through column "J" (see below), gave 1500 cc. of the diisobutylenes boiling at 100–105° (738 mm.) and 500 cc. of residue of triisobutylene and higher polymers. Usually several runs were worked up together.

During the course of the work some diisobutylene was kindly supplied by Dr. Graham Edgar of the Ethyl Gasoline Corporation. This boiled at 98–108° (760 mm.). It had been prepared from material obtained by absorbing cracked refinery gases in sulfuric acid. This diisobutylene was refluxed over metallic sodium and given a preliminary distillation through column "J." Neither in this nor in subsequent distillation was any difference noted between the diisobutylene made in this Laboratory from tertiary butyl alcohol and that made by the Ethyl Gasoline Corporation from cracked gases containing isobutylene.

Description of Columns.¹²—Three columns were used. All were well insulated and were operated with total condensers and variable take-offs. Usually the take-off was adjusted at about 5 cc. per minute and the heat supplied was adjusted to give maximum reflux without flooding the columns.

	Height, cm.	Di- ameter, cm.	Material	Insulation (magnesia pipe cover)	Packing
Column "H"	120	2	Pyrex glass	3.8 cm. with electrical heating	6 × 6 mm. glass rings
Column "J"	180	3.6	Cast iron	8.9 cm.	Same
Column "W"	260	1.8	Brass	5.1 cm.	6 × 6 mm. brass rings

With columns H and J, Pyrex glass flasks were used as stills. These were heated in oil-baths. Column W was fitted with a 1500-cc. brass pot electrically heated. The boiling points were taken on a short Anschütz thermometer with the mercury thread entirely in equilibrium with the condensing vapor.

Distillations.—At first careful fractionations were carried out in the usual way according to the boiling points of the fractions. It was soon found that the refractive indices changed much more rapidly than the boiling points. Thus fractions from different distillations but having similar refractive indices were combined and refractionated. In all the distillations fractions of 50–60 cc. were taken even when the boiling point did not vary. During the early distillations such successive fractions showed changing refractive indices. In later distillations fractions were obtained which on redistillation gave successive fractions with the same boiling points and the same refractive indices.

Since the various fractionations gave over five hundred fractions, it is obviously impossible to give all the details. The fractionations are summarized in the following table. Distillations 1–17 were carried out in column J and distillations 18–29 in column W.

¹² The design of these columns was according to suggestions by M. R. Fenske, who is in charge of the investigations on Pennsylvania petroleum in this Laboratory.

TABLE I
 DISTILLATION DATA

No.	Charge			Bar., mm.	Time, hrs.	Frac- tions taken	Distillate			% Recovered over original ref. ind. range	
	Vol., cc.	Source	n_D^{20}				Important Fractions—	Ref. in l.	Ref. ind., range of all fractions		
1	5000	Crude		739-736	19	18	1670	100.6-100.8			
2	5100	Ethyl Gas. Corp.		721-724	20	18	2475	99-100			
3	5000	Same		724-726	18	24	2442	99.6-100.2			
4	3700	Crude		725-726	10	15	1470	98.8-100.3			
5	6690	Dist. 1-4 main frac- tions, b. p. 99.6 (721) to 100.8° (739)		743-739	27	21	4890	100.4-100.7			
6	815	Dist. 5, Fract. 6, 7, b. p. 100.5° (744)		722-717	5	12	510	99.2 (718)			
7	910	Dist. 5, Fract. 13,14, b. p. 100.6° (738)		731	5	5	465	100.0-100.1			
8	2300	Dist. 1-4, low boiling		730	9	6	880	99.8-99.9			
9	610	Dist. 8, Fract. 2, b. p. 99.8-99.9°		727-728	5	10	412	99.6-99.8	1.4088-90	1.4088-98	
10	510	Dist. 6, Fract. 2		743-742	4	8	304	100.4-100.5	1.4088-90	1.4088-91	
11	465	Dist. 7, Fract. 2		741	3	7	320	100.4-100.5	1.4089-90	1.4088-93	
12	5480	Dist. 1-11	1.4098-1.4138	740-737	22	51	1714	100.8-101.0	1.4100-2	1.4080-1.4142	75
13	1915	Dist. 1-11	1.4091-9	726-730	10	35	1246	99.8-100.1	1.4088-90	1.4084-1.4125	13
							180	100.5-100.8	1.4100- 1.4105		
14	2010	Dist. 12, Fract. 28- 47, 100.0-102.4° (738)	1.4101-31	734	9	21	724	100.7-100.8	1.4100-2	1.4097-1.4150	55
							518	101.6-104.6	1.4120-50		
15	2850	Dist. 5, Fract. 5, 8- 12, Dist. 8, Fract. 3	1.4089-90	734-732	11	27	861	100.0	1.4080-4	1.4080-1.4118	18
							1140	100.0-100.1	1.4085-8		
							434	100.1-100.3	1.4089-91		

TABLE I (Concluded)

No.	Charge			Bar., mm.	Time, hrs.	Frac- tions taken	Distillate				% Recovered over original ref. ind. range	
	Vol., cc.	Source	n_D^{20}				Important Fractions		Ref. ind.	Ref. ind., range of all fractions		
							Vol., cc.	B. p., °C.				
16	965	Dist. 5, Fract. 6, 7, 13, 14, Dist. 8, Fract. 2	1.4089-90	731-732	4	10	785	99.9-100.1	1.4088-90	1.4088-96	15	
17	1980	Dist. 12, Fract. 15-27 Dist. 13, Fract. 29-32 Dist. 14, Fract. 2-5	1.4098-1.4102	737	10	31	919	100.4-100.7	1.4090-4	1.4090-1.4140	20	
18	840	Dist. 12, Fract. 48-9 Dist. 14, Fract. 14-19	1.4112-38	728	6	17	220 210	102.0-104.0 100.8-101.0	1.4120-40 1.4110-	1.4107-52	33	
19	590	Dist. 5, 6, 12, 13, 15, low fractions	1.4080-5	733	11	15	349	100.0-100.1	1.4084- 1.4089	1.4064-1.4108	23	
20	1170	Dist. 15, Fract. 2-13	1.4080-5	726-729	12	21	788	99.7-100.1	1.4086-8	1.4084-90	17	
21	880	Dist. 15, Fract. 14-22	1.4085-9	737-740	10	17	694	100.1-100.2	1.4087-90	1.4085-94	79	
22	950	Dist. 6, Fract. 1 Dist. 9, Fract. 1 Dist. 12, Fract. 2, 3 Dist. 13, Fract. 2-14 Dist. 15, Fract. 23	1.4088-9	732-730	12	19	590	99.9-100.0	1.4082-4	1.4080-1.4128	20	
23	628	Dist. 14, Fract. 10-13 Dist. 17, Fract. 26, 27	1.4105-10	735	6	13	241 133	100.4-100.7 102.0-102.7	1.4090-2 1.4117-33	1.4090-1.4133	8	
24	980	Dist. 12, Fract. 6, 7 Dist. 14, Fract. 1, 8, 9 Dist. 15, Fract. 25 Dist. 17, Fract. 18-25	1.4093-1.4102	731-732	8	16	480 296	100.2-100.5 100.6-102.0	1.4090-1 1.4096- 1.4120	1.4087-1.4135	19	
25	510	Dist. 13, Fract. 15-24	1.4090	734-731	5	11	418	100.0-100.2	1.4085-90	1.4082-1.4120	20	
26	580	Dist. 13, Fract. 25, 26 Dist. 15, Fract. 24 Dist. 17, Fract. 1-7	1.4090-3	733-732	7	12	436	100.0-100.2	1.4087-90	1.4087-1.4133	18	
27	690	Dist. 13, Fract. 27, 28 Dist. 17, Fract. 8-17	1.4093-4	729-728	8	15	457	99.8-100.2	1.4087-92	1.4085-1.4130	13	
28	1020	Dist. 1-17, residues	1.4093-1.4150	728-726	9	16	445	101.4-103.2	1.4120- 1.4152	1.4098-1.4152	81	
29	515	Dist. 22, Fract. 1-10	1.4080-4	737	6	10	357	100-100.2	1.4083-6	1.4181-97	50	

Possible Changes of Diisobutylene on Standing and during Distillation.—Several samples of diisobutylene of various refractive indices were allowed to stand for over a year and then examined again. No change was observed in their refractive indices. This showed that no appreciable polymerization or oxidation had taken place under the conditions used, namely, storage in glass bottles with cork stoppers and exposure to ordinary daylight. The oxidation and polymerization products of diisobutylene all have higher indices of refraction.^{2,3}

In order to determine the possibility of the dissociation of diisobutylene during distillation, a sample of known refractive index was refluxed through column "W" (the tallest of the columns) for six hours with total reflux. Arrangements were made to catch any escaping isobutylene in a solution of bromine in carbon tetrachloride. When the bromine was removed by sodium thiosulfate and the carbon tetrachloride was distilled, no high boiling material was obtained. A blank using known isobutylene showed there was no difficulty in detecting even a small amount of the dibromide, b. p. 146–148° (738 mm.). The material in the pot showed no change in refractive index, thus showing that it contained no dissolved isobutylene formed during the refluxing and that it had not suffered any appreciable change during its contact with the brass column and packing. A small amount of dissolved isobutylene lowers the refractive index of diisobutylene notably.

Separation of Diisobutylene and Triisobutylene.—The possibility of separating these materials by the type of columns used was definitely settled by the following experiment. A large amount of the residues from the fractionation of crude diisobutylene was distilled from an ordinary distilling flask and the 1500 cc. boiling at 160–200° was redistilled through column "H" with the column heated to 150–160°. A fraction amounting to 850 cc. boiled at 173–174° (726 mm.). This was distilled again through column "H" as before. Twenty fractions were taken with boiling points at 738 mm. from 175.5 to 178.8° and refractive indices from 1.4300 to 1.4338. Fractions 2–14 were used for the distillation experiment with diisobutylene. These fractions ranged in boiling point from 175.7 to 176.4° (738 mm.) (corr.) and in refractive index from 1.4300 to 1.4305. A sample of the mixture on distillation through column H gave the following results, 170.6–175°, 8.5 cc.; 175.0–176.2°, 419 cc., n_D^{20} 1.4300; 176.2–176.6° (flask dry), 95 cc., n_D^{20} 1.4308.

Diisobutylene, fractions 14 to 18 of Distillation 20, b. p. 100.0–100.1° (727–729 mm.), n_D^{20} 1.4087–1.4088, was distilled through column "H." Practically all (97%) distilled at 99.8–100.0° (734 mm.) and had a refractive index of 1.4085.

The above diisobutylene (156 cc.) and triisobutylene (156 cc.) were distilled through column "H" with the results given in the following table.

Bar., mm.	Time, min.	B. p., °C.	Fraction	Vol., cc.	Ref. index	% Distilled (total)
733	0	99.6				
	18	99.8	1	4.5	1.4085	1.3
732.5	85	99.8	2	99	1.4086	34.7
	130	99.8	3	17	1.4087	40.4
	190	99.8	4	20	1.4087	47.1
	200	100.0	5a	2		47.7
	235	101.0	5b	6	1.4090	49.8
	Heat on column	245	110.0	6a	4	
	254	127.0	6b	1		
	257	132.0	6c	0.5	1.4099	51.6
	292	171.0	7	7	1.4210	54.0
	314	175.0	8	8	1.4288	56.6
732	328	175.4	9	13	1.4300	61.0
	388	175.8	10	94	1.4300	92.4
	400	175.8	11	22	1.4303	100.0

The flask was dry at the end of the distillation. The hold-up and loss amounted to 14 cc.

Physical Properties.—The boiling points were determined at various pressures near 735 mm. in a Cottrell boiling point apparatus with a standardized Anschütz thermometer having the mercury thread entirely exposed to the vapor. The value of $\Delta p / \Delta$ b. p. for each isomer was found to be about 21.8 mm. per degree C. The boiling points at 760 mm. were calculated from this relation.

The refractive indices were determined to four places with an Abbé refractometer with prism kept at a constant temperature by water from a bath held at 20.0°. Observations taken at different times on the same samples checked within one or two in the fourth decimal place.

When larger amounts of the pure isomers are available they are to be submitted to various physical chemists and physicists to be measured accurately as was done in connection with the classical researches of Edgar, Calingaert and Marker on the isomeric heptanes.

Summary

1. By repeated fractionation through improved laboratory columns of the adiabatic, total condensation, variable take-off type, "diisobutylene" can be separated into 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2, the former being present in much the larger amount.

2. The boiling points, densities and refractive indices of the isomers have been determined.

STATE COLLEGE, PENNSYLVANIA