For example, since the beta structure in sodium palmitate incorporates up to 2.5% water in solid solution with accompanying continuous changes in interplanar spacings and other properties, a similar behavior would be expected in sodium stearate and other beta-forming single or commercial soaps. In addition, Ferguson and Nordsieck have demonstrated[6] the actuality of solid solution among crystalline soaps of different *chain lengths*, including even complex mixtures. It is then reasonable to expect in the sodium soaps, a comprehensive beta phase continuous with respect to both chain length and water content. The possibility of a similar phase continuity should be considered for the omega and delta structures.

Contrasted to this point of view is that of Buerger and his co-workers who have assigned distinct phase designations to each of ten X-ray patterns,[4] some distinguished by relatively slight differences, leading to a phase situation of considerable complexity. That some of this complexity has been introduced needlessly is evident from our more detailed exploration of the beta-zeta relationships, which has revealed a single solid solution phase. Consequently, epsilon, and also the several phases showing pattern resemblances to omega, should be studied further in the hope that simplifying relationships will be discovered there also.

In any case we propose, as a guiding principle, that the number of crystalline soap structures be kept at the minimum consistent with available evidence, in order that the subject of solid soaps may develop with greater simplicity and clarity. The final section of reference 4 with its tentative phase map is an indication of the predicament into which the multiphase concept can lead.

It is not, of course, necessary that each of such basic crystalline structures be capable of forming solid solutions with water. As a matter of fact, the alpha structure seems well established as a hydrate.[15,23,24]

Acknowledgment.—The writers wish to acknowledge the advice of Dr. A. S. Richardson in developing the subject matter of this paper.

Summary

On the basis of X-ray, vapor pressure and microscopic evidence, certain minor variations previously encountered among X-ray patterns of beta sodium palmitate are accounted for by the existence of a beta solid solution phase extending at room temperature from about 0.2 to 2.5% water.

This beta structure is shown to embrace previous beta palmitates and stearates as well as the zeta, and possibly the epsilon, phase. Beta and zeta are therefore not hydrates of fixed composition.

Some justification is offered for keeping the number of distinct crystalline soap structures as few as consistent with available evidence.

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(23) M. J. Buerger, *Proc. Nat. Acad. Sci., U. S.* **28**, 529–535 (1942).

(24) M. J. Buerger, *Am. Mineral.*, **30**, 551–571 (1945).

IVORYDALE, OHIO RECEIVED AUGUST 5, 1946

[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES, A DIVISION OF SOCONY-VACUUM OIL CO., INC., RESEARCH AND DEVELOPMENT DEPARTMENT]

Decenes Formed from *t*-Amyl Alcohol and from 2-Methyl-2-butene. Composition of the Hydrogenated Products

BY GEORGE C. JOHNSON

The formation of decenes from *t*-amyl, *i*-amyl and optically active amyl alcohol and the dimerization of isopentenes in the presence of catalysts was investigated for a century.[1–5] However, after this time the structures of the resulting decenes remained in doubt.[6] The closely similar reaction of the formation of decenes from methyl *i*-propyl carbinol in the presence of sulfuric acid was studied in greater detail.[6–8] In an effort to establish the decene structures more definitely the present studies have been undertaken. In these studies decenes have been formed from *t*-amyl alcohol in the presence of sulfuric acid and from 2-methyl-2-butene in the presence of an alumina–silica catalyst.

The procedure for investigating the structures consisted of the hydrogenation of the decenes to decanes and subsequent analysis of the decanes by efficient fractional distillation accompanied by the determination of the physical properties of the fractions. This same procedure has been used in the studies of similar nonenes prepared by the reaction of *t*-butyl alcohol with *t*-amyl alcohol and of *i*-butene with 2-methyl-2-butene.[9]

Experimental

Reaction of *t*-Amyl Alcohol in the Presence of Sulfuric Acid.—The material used for this study was the decene fraction formed when *t*-amyl alcohol and *t*-butyl alcohol reacted together with the object of making the nonenes.[9]

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(1) Cahours, *Ann.*, **30**, 288 (1839).

(2) Schneider, *ibid.*, **157**, 185 (1871).

(3) Schindelmeiser, *Chem. Ztg.*, **45**, 566 (1921).

(4) Norris and Joubert, THIS JOURNAL, **49**, 873 (1927).

(5) Lebedev and Vinogradov-Volzynski, *J. Russ. Phys.-Chem. Soc.*, **60**, 441 (1928).

(6) Kline, Drake and Rose, THIS JOURNAL, **56**, 2076 (1934); Kline and Drake, *J. Research Natl. Bur. Standards*, **13**, 705 (1934).

(7) Rose, Dissertation, University of Maryland, 1934.

(8) Whitmore and Mosher, THIS JOURNAL, **63**, 1120 (1941); **68**, 281 (1946).

(9) Johnson and Fawcett, *ibid.*, **68**, 1416 (1946).

(10) Whitmore, *ibid.*, **54**, 3274 (1932); *Ind. Eng. Chem.*, **26**, 94 (1934); Whitmore and Mixon, THIS JOURNAL, **63**, 1460 (1941).

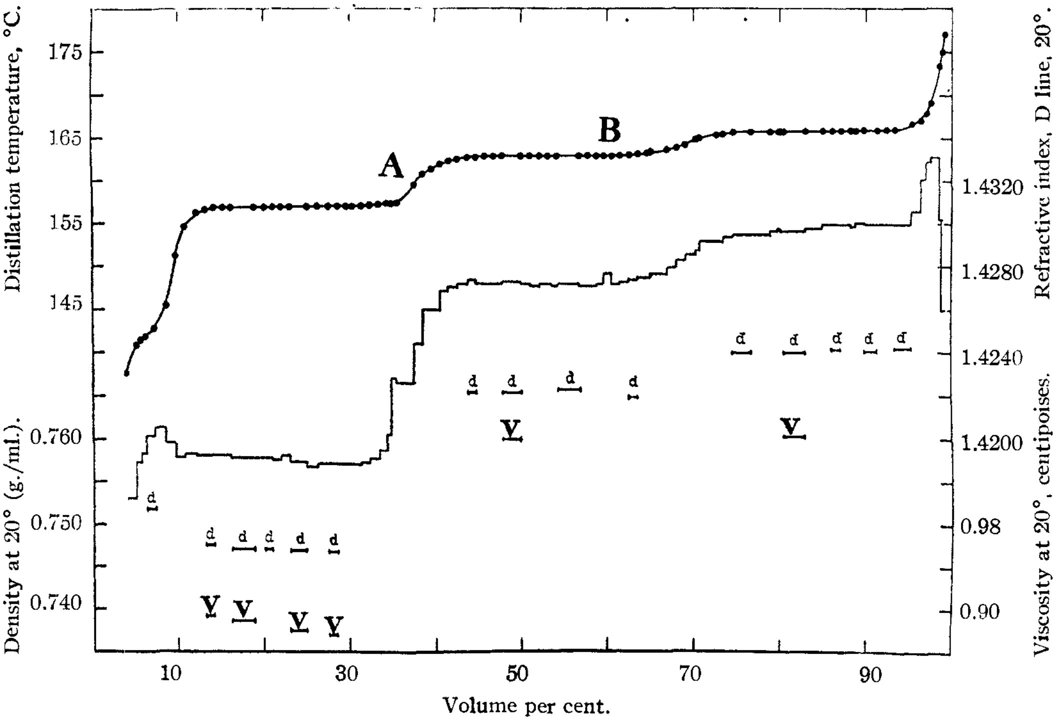

Fig. 1.—Distillation curve for the hydrogenated products of the decenes formed from *t*-amyl alcohol in the presence of sulfuric acid: top curve, temperatures; second curve, refractive indices; d indicates density; v indicates viscosity; A and B, distillation interrupted.

14.8 kg. of *t*-butyl alcohol and 17.6 kg. of *t*-amyl alcohol were mixed and added with stirring to 56.7 kg. of 67.2% by weight sulfuric acid kept below 25°. The reaction was conducted in a water-jacketed 125-liter glass-lined kettle equipped with water-cooled reflux and take-off condensers arranged in series. A homogeneous solution resulted. Counting the water formed chemically from the alcohols as contributing to the dilution of the acid, the acid concentration was 59.6% by weight.

The mixture was then heated at a slow rate and gently stirred. When *i*-pentenes were observed in the reflux condenser, the heating was stopped momentarily until the reflux almost disappeared. As hydrocarbon was formed it rose to the top layer and was only slightly contacted with the acid thereafter. A final temperature of 75° was reached in four hours. The stirrer was turned off and the mixture allowed to cool and stratify. 64.2 kg. of the acid layer was drawn off, a gain of 0.3 kg. over the sum of the amount of acid and of the chemically-formed water from the alcohols charged, indicating a small amount of carbon compounds still present in the acid layer. The hydrocarbon layer was washed with water and neutralized with dilute sodium hydroxide solution; 24.2 kg. of hydrocarbon, representing a yield of 96.0% of theoretical, was recovered; 0.7 kg. of material was lost. Nine such runs were made and the hydrocarbons combined.

The hydrocarbons were distilled in a column of 40 theoretical plates using a 10:1 reflux ratio. The decene fraction, 140–170°, comprised 12.2% by weight of the polymer mixture. The main product was 47.0% nonenes, 120–140°. The decene fraction was hydrogenated in a continuous vapor-phase apparatus at 150–180° and 1 atm. with a nickel hydrogenation catalyst. One part by volume of water was charged with each two parts of hydrocarbon, since this quantity of water minimized cracking of the hydrocarbon. The decanes were distilled using 20:1 reflux ratio in a column of 45 theoretical plates, 3.5% by volume of low boiling product, *i*-pentane, being obtained. A fraction of decanes at 155–159° was observed and a larger fraction at 163–168°. A bromine titration showed the absence of olefins.

The analytical distillation was made in a 95-theoretical plate column using 2500 cc. of the decanes, 132–169°, to which was added 500 cc. of dodecanes, 175–178° (uncor.), made as a by-product in the same preparation from *t*-butyl alcohol. The dodecanes were added in order that the decanes might be completely distilled. The distillation and the determination of properties of the fractions were made as described previously.[9]

Results

The results of the analytical distillation of the decanes from the sulfuric acid reaction are plotted in Fig. 1. The distillation began with a nonane—2,3,3,4-tetramethylpentane—and then showed a long decane plateau at 156–157°. The material distilling over at the plateau temperature was not a single decane but rather two decanes (I and II) as shown by a decisive decrease in viscosity of successive fractions and by infrared absorption spectrograms of the fractions. The distillation temperature then rose to a second plateau (decane III) at about 163° and a third plateau (decane IV) at 166°, each of almost uniform refractive index. A small amount of a decane (V) of increased refractive index occurred at the end of the decane distillation. The temperature then rose and the refractive index fell to the first dodecane fraction—2,2,4,6,6-pentamethylheptane. The occurrence of decane V was confirmed by infrared absorption spectrograms, which showed a compound other than IV and 2,2,4,6,6-pentamethylheptane in the high refractive index cuts at the end of the decane portion.

Two steps were used for determining the identity of the five decanes. First, a polymerization theory based very largely on that of Whitmore[10] but defining in greater detail the nature of the carbon skeleton shifts which occur during the polymerization reaction, indicated that the expected products should be 3,3,5-trimethylheptane, 2,2,3,4-tetramethylhexane, 2,3,3,4-tetramethylhexane, 2,3,4,4-tetramethylhexane, 2,3,4-trimethyl-3-ethylpentane and 2,2,4-trimethyl-3-ethylpentane. Second, the values of the decane properties estimated by Francis,[11] together with the limited number of experimental values, were used to prepare charts of boiling point versus refractive index and of boiling point versus density. The values for all 75 isomeric decanes were placed on these charts. The observed physical properties of fractions from the analytical distillation were also plotted. They appeared at positions of relatively high refractive index or density for a given boiling point, making it possible to eliminate the many isomers which had a relatively low refractive index or density as possible observed decanes. Furthermore, the values of the observed properties were entirely consistent with those of the decanes predicted as present. Decane I was 2,2,3,4-tetramethylhexane and II was 3,3,5-trimethylheptane, their combined volume percentage being 31.1. Decane III was 2,3,4,4-tetramethylhexane, 36.9%; IV was 2,3,3,4-tetramethylhexane, 30.3% and V was 2,3,4-trimethyl-3-ethylpentane, 1.7%. The sixth decane—2,2,4-trimethyl-3-ethylpentane—was not found.

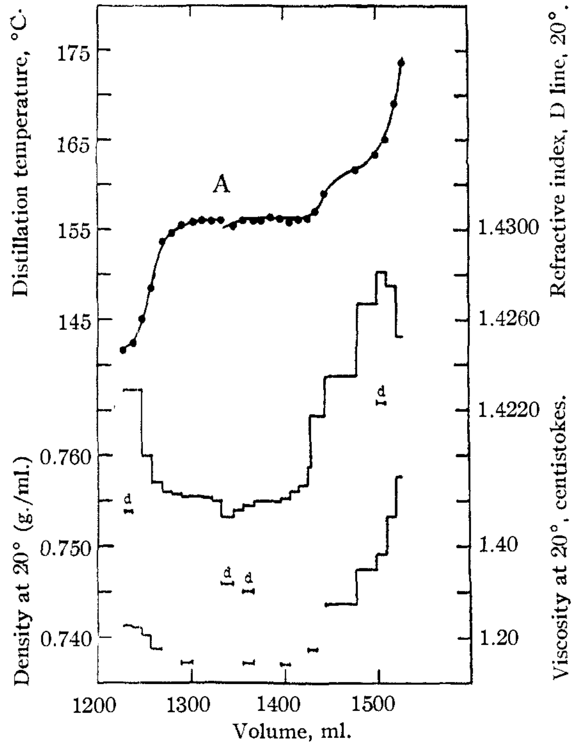

Fig. 2.—Distillation curve for the hydrogenated products of the decenes formed from 2-methyl-2-butene in the presence of an alumina–silica catalyst: top curve, temperature; second curve, refractive indices; d indicates density; lower incomplete line, viscosity; A, distillation interrupted.

A plot of the viscosity as a function of branching for all available paraffins from the pentanes through undecanes indicated that 2,2,3,4-tetramethylhexane is more viscous than 3,3,5-trimethylheptane. On this basis it was concluded that the early part of the first plateau contained relatively more of the tetramethylhexane than the latter part.

Dimerization of 2-Methyl-2-butene in the Presence of an Alumina–Silica Catalyst.—The preparation of these decanes has been described[9] and their analytical distillation is a continuation of the nonane distillation already reported.

The results of the distillation are plotted in Fig. 2. After the distillation of the last nonane—2,3,3,4-tetramethylpentane—the distilling temperature rose to a plateau at 156–157° and remained there for most of the decane fraction, rising to a shoulder at 159–166° before going on to higher fractions. The plateau fractions had an almost constant index of refraction, density, and viscosity.

The decanes present in the alumina–silica product were compared with the decanes from the sulfuric acid product by measurement of their infrared absorptions. These established two facts: (1) The major component of the plateau was the same as the decane occurring in the latter portion of the first plateau of the acid product—*i. e.*, 3,3,5-trimethylheptane; (2) the decanes present in the shoulder were the same as the decanes III and IV found with the acid—2,3,4,4-tetramethylhexane and 2,3,3,4-tetramethylhexane.

Physical Properties of Decanes.—The physical properties of the five decanes found during this work have been collected in Table I together with earlier estimations and determinations of these properties. The physical properties of 2,2,4,6,6-pentamethylheptane, the next higher boiling material in these reactions, have been included in the table. The values found for the properties of this dodecane confirm earlier work.

The values of the decane properties are concordant except for 3,3,5-trimethylheptane. A preparation of this decane by an independent method and a determination of its physical properties would serve to clarify several doubtful points.

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[11] Francis, *Ind. Eng. Chem.*, **35**, 442 (1943); **36**, 256 (1944). Dr. Francis kindly re-calculated the properties of several isomers of interest giving consideration to additional experimental data which have become available.

TABLE I

PHYSICAL PROPERTIES OF FIVE DECANES AND A DODECANE

Compound	B. p., °C.	d^{20}_4	$n^{20}D$	η^{20}	Ref.
2,2,3,4-Tetramethylhexane	156.6	0.7547	1.4324		11
	156.5	.7548^{a}	1.4224^{a}		12
	156.6				This work
3,3,5-Trimethylheptane	155.2	.7418	1.4171		11
	159.1	.7553^{a}	1.4230^{a}		12
	156.8	.7450^{c}	1.4178^{c}	0.851^{c}	This work
2,3,4,4-Tetramethylhexane	161.0	.7623	1.4274		11
	162.8	.7654	1.4272	1.060	This work
2,3,3,4-Tetramethylhexane	164.3	.7690	1.4306		11
	165.7	.7700	1.4297	1.063	This work
2,3,4-Trimethyl-3-ethyl pentane	167.8	.7761	1.4335		11
	167		1.4331^{d}		This work
2,2,4,6,6-Pentamethylheptane	177.2	.7468	1.4191		13
	179–180		1.4183^{b}		14
	175–176	.7487	1.4218		15
	177.8	.7463	1.4194		This work

[a] Corrected to 20 from 25°. [b] Corrected to 20 from 30°. [c] The listed values are for a material contaminated by an unknown but small amt. of material of higher density, refractive index and viscosity. [d] The fraction examined was contaminated with a small but unknown amount of material of lower refractive index.

Discussion

Of the decanes found in this study, the decene parent of one of them—2,3,4,4-tetramethyl-2-hexene was tentatively identified by Schindelmeiser[3] and by Norris and Joubert[4] in the dimer of 2-methyl-2-butene formed in the presence of sulfuric acid.

In the decenes formed from methyl-*i*-propylcarbinol Kline, Drake and Rose[6] found 2,2,3,4-tetramethyl-4-hexene and 3,3,5-trimethyl-5-heptene. These observations were confirmed by Whitmore and Mosher,[8] who searched for other decenes but concluded that only these two were present. Furthermore, these same two decenes were found in the Sharples diamylenes made by the action of sulfuric acid on a mixture of pentenes, mostly 2-methyl-2-butene and 2-pentene.[7]

The decenes from methyl-*i*-propylcarbinol are expected[8] to be the same as those from *t*-amyl alcohol. In the present study the two decanes expected from the methyl-*i*-propylcarbinol work were found. In addition three other decanes, amounting to 68.9% by volume of the total decanes, were present.

As a preliminary effort to assign reasons for the variant results it is agreed first that the decenes formed from the methyl-*i*-propylcarbinol would be expected to be the same as those from *t*-amyl alcohol. Second, the amounts of the various decenes would be expected to vary, not so much because of the difference in the alcohols, but because more concentrated sulfuric acid (68.7% *vs.* 59.6%) was used by the earlier workers. This greater strength of acid would be expected to lead to more of the re-arranged decenes in the products of the earlier workers. Third, it is suggested that certain decenes actually present were missed by earlier workers due to the selectivity of the ozonolysis reaction used by them in establishing structure. The selectivity of the ozonolysis reaction has been shown previously.[16,17] The decenes which it is now believed to have been present but undiscovered in the product of the earlier workers are of a type which reacts least readily with ozone and are most likely to be missed. For example, Wheeler[16] found 2,3,3,4-tetramethyl-1-pentene to resist ozonolysis. In the previous work about 40% of the decenes remained unreacted in the ozonolysis reaction.

As corollaries to these suggestions one must conclude that at least one of the two close boiling decene cuts found by both earlier groups was not a pure compound as assumed but a mixture and furthermore that at least one of the two decanes found by Drake and Welsh[12] was a mixture. Hence several materials reported earlier as pure are now questioned and their properties are in doubt. The identity of one of them—3,3,5-trimethylheptane—has already been questioned by Francis.[11]

Acknowledgment.—The author expresses his appreciation to Mr. Frank S. Fawcett for his aid in the decane analyses and to Mr. J. G. Ehlers for his spectroscopic work.

Summary

1. The decanes formed by hydrogenating the decenes made from *t*-amyl alcohol in the presence of 59.6% by weight sulfuric acid below 75° are 2,2,3,4-tetramethylhexane and 3,3,5-trimethylheptane together 31.1% by volume; 2,3,4,4-tetramethylhexane 36.9%; 2,3,3,4-tetramethylhexane 30.3%; 2,3,4-trimethyl-3-ethylpentane 1.7%.

2. The decanes formed by hydrogenating the dimer of 2-methyl-2-butene formed in the presence of an alumina–silica catalyst at 110° are mostly 3,3,5-trimethylheptane with lesser amounts of 2,3,4,4-tetramethylhexane and 2,3,3,4-tetramethylhexane.

3. Physical properties of five decanes and one dodecane are reported.

PAULSBORO, N. J. RECEIVED SEPTEMBER 13, 1946

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(12) Drake and Welsh, THIS JOURNAL, **60**, 488 (1938).

(13) Meyer, Thesis, Pennsylvania State, 1941.

(14) Bartlett, Fraser and Woodward, THIS JOURNAL, **63**, 497 (1941).

(15) Petrov and Kaplan, *J. Gen. Chem.* U. S. S. R., **12**, 99 (1942).

(16) Wheeler, Thesis, Pennsylvania State College, 1941.

(17) Whitmore and co-workers, THIS JOURNAL, **63**, 2035 (1941).