stable or on the stable curve. These points, which are grouped around 21% silver sulfate and 76.5% sulfuric acid, may indicate one or both of the invariant points between the two forms of the bisulfate and the 1:2 addition compound. Kendall and Davidson's measurements on the binary system sulfuric acid–silver sulfate,[4] show that this 1:2 salt is the stable solid phase at 25°. Its solubility, calculated from their data to be 24% silver sulfate by weight, should be represented by a point on the silver sulfate–sulfuric acid base of the ternary diagram at 25°, and from that point there should be a short but definite solubility curve for this salt. This curve, however, was not experimentally realizable in this study, which was limited to the use of 98% sulfuric acid, making it impossible to prepare complexes with compositions close enough to the base of the triangle to give rise to the 1:2 salt. Solid residue analyses always showed the solid phase to be the 1:1 salt.

From a plot of Kendall and Davidson's data it was possible to estimate by extrapolation the metastable solubilities, at 25°, in pure sulfuric acid, of the alpha and beta forms of the bisulfate. The value for the alpha was estimated to be equivalent to 28.5% silver sulfate by weight, and that for the beta 29.5% silver sulfate. If these points are marked off on the silver sulfate–sulfuric acid side of the ternary diagram, it can be seen that they represent the points to which the bisulfate solubility curves would most likely have extended had they not been interrupted by the formation of the 1:2 compound in the highest concentrations of sulfuric acid.

Summary

1. The ternary system Ag_2SO_4–H_2SO_4–H_2O has been studied at 25° to the limit of 98% sulfuric acid by weight.

2. The solid phases observed were the normal sulfate, Ag_2SO_4, and the bisulfate, $AgHSO_4$.

3. Two solubility curves have been obtained for the 1:1 addition compound, the stable solubility curve being that for the alpha form of the bisulfate, the metastable curve being that for the beta form, both forms already having been reported by Kendall and Davidson.[4]

4. A stable and metastable invariant point have been determined for the crossing of the bisulfate solubility curves with that for the normal sulfate.

5. An indication of an invariant point between the bisulfate curves and the solubility curve for the salt $Ag_2SO_4 \cdot 2H_2SO_4$ has been obtained, but the 1:2 addition compound itself was not observed in this investigation, because of the limitation in the concentration of the sulfuric acid used.

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

Inter-polymerization of Isobutene and 2-Methyl-2-butene Using an Alumina–Silica Catalyst. Composition of the Hydrogenated Nonenes

BY GEORGE C. JOHNSON AND FRANK S. FAWCETT

When isobutene and 2-methyl-2-butene react in the presence of a solid catalyst composed of alumina and silica at temperatures of the order of 110°, the main product is a mixture of nonenes. Other products are octenes, decenes and trimers. A similar nonene product is formed in the reaction of *t*-butyl alcohol with *t*-amyl alcohol in the presence of sulfuric acid. The *t*-butyl alcohol is equivalent to isobutene and the *t*-amyl alcohol is equivalent to 2-methyl-2-butene or to 2-methyl-1-butene in those cases where the reactants are first dissolved in the acid.

The nonanes formed by hydrogenating the nonenes have special properties as a fuel for internal combustion engines. The power output of the engine under rich-mixture conditions—*i.e.*, high fuel–air ratios—is remarkably high. Too, the power delivered by the engine is unusually sensitive to the inlet air temperature when the nonanes are used as the fuel. These special properties depend upon the composition of the nonanes, especially upon the total content of tetramethylpentanes, and the composition depends in turn upon the method of carrying out the reaction.

The composition of the nonane mixture has been determined by distilling the mixture into fractions with an efficient column, by measuring the physical properties of these fractions and then comparing these properties with those of the 35 isomeric nonanes.

Alumina–silica catalysts have been used before to polymerize olefins[1–6] and some studies of the

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(1) Gurvich, *Kolloid-Z.*, **11**, 17 (1912); *J. Russ. Phys.-Chem. Soc.*, **47**, 827 (1915); *Z. physik. Chem.*, **A107**, 235 (1923).

(2) Lebedev and Filonenko, *Ber.*, **58**, 163 (1925).

(3) Van Winkle, *J. Am. Pharm. Assoc.*, **17**, 544 (1928).

(4) Gayer, *Ind. Eng. Chem.*, **25**, 1122 (1933).

(5) Lebedev and Borgman, *J. Gen. Chem.* (U. S. S. R.), **5**, 1595 (1935).

(6) Houdry, Burt, Pew and Peters, *Natl. Petroleum News*, **30**, R570 (1938).

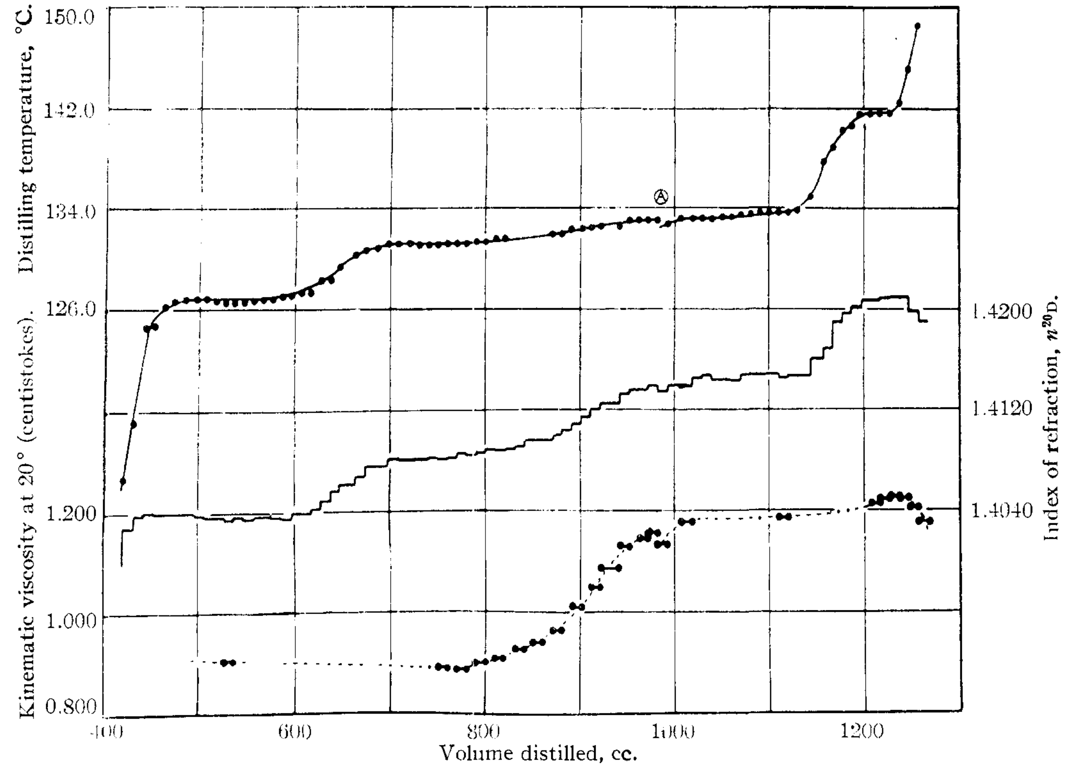

Fig. 1 —Top curve, the distillation temperature of the nonanes as a function of volume distilled; middle curve, the indices of refraction of the fractions; lower curve, kinematic viscosity of selected fractions; A, the distillation was interrupted for one day.

structures of the resultant polymers have been made.[7-10]

Experimental

Materials.—Matheson commercial 95% isobutene was used without further treatment. This isobutene contains small amounts of 1-butene and 2-butene as polymerizable impurities. The 2-methyl-2-butene was made by the dehydration of Sharples commercial *t*-amyl alcohol in the presence of 35–45% by weight sulfuric acid at 80°. In this preparation 2-methyl-1-butene (b. p. 31.1°) was also formed and was separated by distillation from the 2-methyl-2-butene (b. p. 38.5°). The catalyst was fresh Socony–Vacuum alumina–silica bead cracking catalyst[11] made during the first days of commercial production. Beads retained on an 8-mesh sieve were used.

Preparation of Nonanes.—The hydrocarbon charge was made from equal weights of isobutene and 2-methyl-2-butene. This represents a mole ratio of 1.25:1.00. The charge was pumped by displacement with ethylene glycol at a rate of 1.0 liter of liquid per hour and at 500 lb./sq. in. gage pressure through a preheat coil and then through 142 g. of catalyst filling a 200-cc. reactor. The oil-bath surrounding the preheat coil and reactor was maintained at 67–88° (average 76°). The reactor temperature varied from 98 to 128° (average 112°) during the 6.5-hour run. The gain in weight of catalyst was 49 g. A recovery of 97.5% of the charge was made.

The entire polymer was hydrogenated in a continuous vapor-phase apparatus over a nickel catalyst at about 160° and one atmosphere pressure. An equal weight of water was added with the hydrocarbon to minimize cracking. The hydrogenated product was distilled to 42° in a column of about 25 theoretical plates to remove 8.2% of material boiling mainly at 28° and identified as 2-methylbutane. The residue was used for the analytical distillation.

Analytical Distillation.—The hydrogenated polymer was distilled with a total condensation, variable take-off column of about 95 theoretical plates. A 232 × 2.0 cm. section was packed with 1.25-turn stainless steel helices of 0.24 cm. diameter made from No. 30 B. & S. wire. A reflux ratio above 120:1 was used. Fractions were taken each 10 cc. (about 1% of total charge). For each fraction the index of refraction (n^{20}D) was measured. For certain fractions the density (d^{20}_4), kinematic viscosity at 20° and Cottrell boiling point were measured. A plot of the distilling temperatures, indices of refraction and viscosities is shown on Fig. 1. The yields of the molecular weight groups were: below octanes, < 91°, 0.4 volume %; octanes, 91–109°, 16.9%; nonanes, 109–148°, 35.4%; decanes, 148–167°, 11.3%; residue, > 167°, 36.0%.

Other physical properties which were determined were:

Volume range, cc.	Cottrell boiling point, °C.	Density, d^{20}_4
527–537	...	0.7163
537–547	126.7	....
760–770	130.9	....
770–780	...	.7259
1039–1050	...	.7387
1050–1060	...	.7391
1060–1070	133.0	....
1110–1120	...	.7391
1217–1227	141.4	....
1227–1237	...	.7538

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(7) Lebedev and Kobliansky, *Ber.*, **63**, 103 (1930).

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Infrared Data.—Ten distillate fractions from plateaus and transitions were selected for analysis by means of infrared absorption spectra. Table I shows the fractions taken, their boiling ranges and their compositions as determined by infrared analysis. Each of the values in the table has an uncertainty of 5–10% of the value itself. In each case the absorption spectrum of the individual fraction was compared with the spectra of known nonanes.[12]

TABLE I

INFRARED ANALYSIS OF THE NONANES

The letter P indicates that the compound was present. The dots indicate that the compound was not found, though a special examination was made for its presence.

Volume range, cc.	Boiling range, °C.	2,2,3-Trimethylpentane	2,3,4-Trimethylpentane	2,2,4-Trimethylhexane	Olefins	2,4,4-Trimethylhexane	2,2,3,4-Tetramethylpentane	Unknown compounds	2,3,3,4-Tetramethylpentane
421–432	112.7–117.1	15	45	30	5	..			
443–453	124.5–124.7	..	12	80	8	..			
527–537	126.5–126.5		..	99		..			
674–684	130.6–130.8		..	3		97	..		
770–780	131.1–131.1					97	3		
952–962	133.0–133.0					5	90	P	..
1050–1060	133.3–133.3					..	95	P	..
1110–1120	133.6–133.6					..	95	P	..
1207–1217	141.5–141.6					..	3	P	92
1227–1237	141.6–142.4						..	P	90

Results.—The assignment of the composition was made by considering carefully the physical properties of the fractions. The summarized physical properties of the nonanes[13] and plots of the refractive index *versus* boiling point, viscosity *versus* boiling point and density *versus* boiling point were useful in making this assignment. The infrared analyses were used to confirm the composition assigned on the basis of the other physical properties and to insure that no other nonanes were present in large amounts. The viscosity data were especially useful for distinguishing between 2,4,4-trimethylhexane and 2,2,-3,4-tetramethylpentane.

The nonane composition was

2,2,4-Trimethylhexane	29% by volume
2,4,4-Trimethylhexane	30
2,2,3,4-Tetramethylpentane	31
2,3,3,4-Tetramethylpentane	9
Unknown	1
	100

The octane fraction distilled almost entirely at 99.0–99.8° and an infrared analysis of the mid-portion showed it to be pure 2,2,4-trimethylpentane. Its physical properties were: b. p. 99.1°, d^{20}_4 0.6919, $n^{20}\text{D}$ 1.3914, η_{20} 0.00502 poise. These values agree closely with the literature data.[14–16] Small amounts of 2,3,4- and 2,2,3-trimethylpentane were found in the transition fractions between the octanes and nonanes.

The physical properties of the four nonanes determined during this study are compared in Table II with the values from the literature.

TABLE II

PHYSICAL PROPERTIES OF FOUR NONANES

Compound	B. p., °C.	d^{20}_4	$n^{20}\text{D}$	η^{20}	Reference
2,2,4-Trimethylhexane	126.5	0.7154	1.4031	....	21
	126.5	.7156	1.4033	....	22
	126.6	.7159	1.4034	0.00651	19
	126.7	.7163	1.4034	.00648	This work
2,4,4-Trimethylhexane	131.1	.7271	1.4098	....	17
	130	.7196	1.4081	.....	18
	131.3	.7290	1.4098	.00668	19
	130.8	.7231	1.4068	.....	20
	130.9	.7255	1.4084	.00638	This work
2,2,3,4-Tetramethylpentane	133.0	.7390	1.4146	.....	22
	133.0	.7394	1.4146	.00892	19
	133.0	.7391	1.4144	.00877	This work
2,3,3,4-Tetramethylpentane	141.5	.7547	1.4220	.....	22
	141.2	.7550	1.4222	.00972	19
	141.4	> .7538	>1.4209	>.00925	This work

Use of Sulfuric Acid as Catalyst.—The same analytical procedure was used to determine the composition of the nonane fraction resulting from the hydrogenated nonenes formed by the interpolymerization of *t*-butyl alcohol with *t*-amyl alcohol in the presence of 60.2% by weight sulfuric acid below 80°.

The nonane fraction was composed of 2,2,4-trimethylhexane 13%; 2,4,4-trimethylhexane 29%; 2,2,3,4-tetramethylpentane 41%; 2,3,3,4-tetramethylpentane 17%; and only traces of other nonanes.

This reaction was studied earlier by other workers. Whitmore and Mixon[23] examined the structure of the nonenes by ozonolysis, fractionation of the oxidation products by distillation, preparation of the 2,4-dinitrophenylhydrazones of selected fractions, recrystallization of the solid products to steady melting points, and the determination of mixed melting points of these derivatives with similar derivatives of suspected oxidation products prepared in other ways. The composition of the nonenes was assigned as: 2,3,4,4-tetramethyl-1-pentene 50%; 2,3,4,4-tetramethyl-2-pentene 10%; 3,5,5-trimethyl-2-hexene 23%; 3,5,5-trimethyl-3-hexene 5%; 2,4,4-trimethyl-2-hexene 10% and others 2%. Had these olefins been hydrogenated quantitatively the nonanes would have been 2,2,3,4-tetramethylpentane 60%; 2,2,4-trimethylhexane 28%; 2,4,4-trimethylhexane 10%; others 2%.

[12] American Petroleum Institute Research Project 44 at the National Bureau of Standards. Catalog of Infrared Spectrograms. Serial no. 130, 2,2,4-trimethylhexane; no. 133, 2,2,3,4-tetramethylpentane; no. 134, 2,3,3,4-tetramethylpentane; no. 363, 2,4,4-trimethylhexane. These four spectrograms were contributed by the Socony–Vacuum Oil Co.

[13] Our own collection of physical properties was used. The values are in substantial agreement with those listed in ref. 22.

[14] Smyth and Stoops, THIS JOURNAL, **50**, 1883 (1928).

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[16] Brooks, Howard and Crafton, *J. Research Natl. Bur. Standards*, **24**, 33 (1940).

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[21] Brooks, *J. Research Natl. Bur. Standards*, **19**, 319 (1937).

[22] American Petroleum Institute Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table no. 4a, Paraffins, C_9, June 30, 1945.

[23] Whitmore and Mixon, THIS JOURNAL, **63**, 1460 (1941).

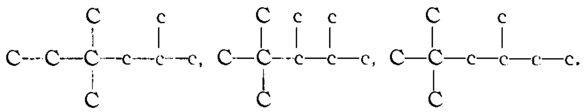
Deanesly and Wachter[24] found the nonene fraction to be composed for the most part of the same three major nonenes found by Whitmore and Mixon. The method of identification was not described.

In continuing the work of Whitmore and Mixon, Wheeler[25] tentatively identified 7% of 2,3,3,4-tetramethyl-1-pentene and a lesser amount of 3,4,4-trimethyl-2-hexene in addition to otherwise confirming their work. The 2,3,3,4-tetramethyl-1-pentene was found in the portion of the nonenes resisting ozonolysis.

The nonanes found in the present study are the same as those expected on the basis of earlier work. The percentage distribution differs, however. This is attributed partly to the difficulty in the ozonolysis procedure brought about by the selectivity in this reaction, as noted especially by the finding of one nonene largely in the unozonized portion. Also there was an important difference in preparation. Whitmore and Mixon obtained 30% isopentenes in their polymer whereas this by-product yield was held to 3% in the present study. A series of experiments showed that isopentene production was sensitive to acid concentration and was minimized by heating the mixture of reactants and catalyst slowly from room temperature to the polymerization temperature. The acid concentration used here was 60.2% by weight sulfuric acid, considering the chemical water derivable from the alcohols as contributing to the dilution of the acid. On the same basis a recomputation of the strength of acid used by Whitmore and Mixon shows 57.6%.

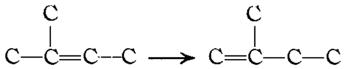
Consideration of the mechanism[23,26,27] of the polymerization reaction indicates that the formation of isopentenes should lead to relatively less of the 2,4,4-trimethylhexane structure in the Whitmore and Mixon product than in the present product. This was found to be the case.

Mechanism of the Reaction.—A proposed mechanism for the polymerization of olefins in the presence of alumina–silica catalysts must account for the following phenomena: 1. Both interpolymerization and self-polymerization exist. Dimers of isobutene and of 2-methyl-2-butene are formed as well as their interdimer. 2. Skeleton isomerization occurs as part of the polymerization. The 2,3,3,4-tetramethylpentane structure can be formed only with the breaking of a carbon–carbon bond. 3. Schematically the reaction consists of the union of the tertiary carbon atom of one molecule with a primary or secondary atom of the other molecule, as



$$C{-}C{-}\underset{C}{\overset{C}{C}}{-}c{-}\overset{c}{c}{-}c,\quad C{-}\underset{C}{\overset{C}{C}}{-}\overset{c}{c}{-}\overset{c}{c}{-}c,\quad C{-}\underset{C}{\overset{C}{C}}{-}c{-}\overset{c}{c}{-}c{-}c.$$

In the above, both the isobutene and the 2-methyl-2-butene provide the tertiary carbon atom. 4. The link in one product, *i.e.*, 2,2,4-trimethylhexane, involves a carbon atom not originally doubly bonded. This suggests that double-bond isomerization occurs preliminary to the polymerization:



$$C{-}\overset{C}{C}{=}C{-}C \longrightarrow C{=}\overset{C}{C}{-}C{-}C$$

The close similarity in the composition of the products formed with alumina–silica and sulfuric acid as catalysts suggests strongly that an acid-type catalysis also occurs with alumina-silica. We suggest that the alumina–silica functions in a manner analogous to that already discussed by Whitmore and Meunier[28] in the case of boron trifluoride. This mechanism covers the four requirements which were listed above and leads one to predict the nonanes to be the four found. In all of our considerations of acid catalyzed polymerizations we have found the mechanism suggested by Whitmore to be more generally valid than the mechanisms or schemes suggested by others.[29–34]

Acknowledgment.—The authors wish to express their appreciation to Mr. E. B. Backensto, who made the polymer; to Mr. W. H. Lang, who made the nonane distillation; and to Mr. J. G. Ehlers, who made the infrared analyses.

Summary

1. The inter-polymerization of isobutene with 2-methyl-2-butene in the presence of an alumina–silica catalyst at 110° and 500 lb./sq. in. gage pressure leads to a mixture of nonenes which on hydrogenation yield 2,2,4-trimethylhexane 29%; 2,4,4-trimethylhexane 30%; 2,2,3,4-tetramethylpentane 31%, 2,3,3,4-tetramethylpentane 9%; and about 1% of unidentified compounds.

2. Though the proportions differ, these nonanes are the same as those resulting from the reaction of *t*-butyl alcohol with *t*-amyl alcohol in the presence of 60% by weight sulfuric acid below 80°.

3. Physical properties of four nonanes are reported.

4. The mechanism of the polymerization reaction in the presence of alumina–silica catalysts is indicated.

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