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Reaction of Propene with Isoolefins in the Presence of Sulfuric Acid

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It was previously¹ shown that under the influence of sulfuric acid aliphatic olefins containing four or more carbon atoms undergo conjunct polymerization yielding, in addition to polymeric olefins, paraffinic and cyclic hydrocarbons. The predominance of the one or other type of hydrocarbon depends greatly upon the concentration and amount of sulfuric acid used.

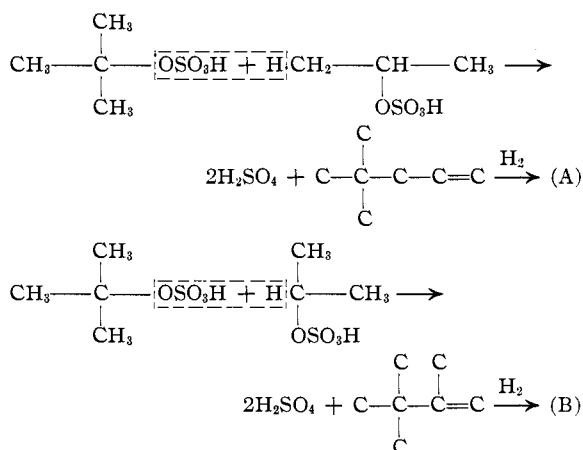
Propene was found to be more resistant to polymerization for when contacted under atmospheric pressure with 96% sulfuric acid at 0 and 25°, it yielded chiefly isopropyl sulfates and only negligible amounts of hydrocarbons. The addition of cupric sulfate or mercuric sulfate to the sulfuric acid did not promote the polymerization of propene.²

However, when mixed with more reactive olefins such as isobutene or isopentenes and then contacted with sulfuric acid, the propene reacted with the other olefins to yield among other products heptenes and octenes, respectively. No hydrocarbons corresponding to the dimer or trimer of propene were found in the reaction product. With straight chain olefins such as *n*-butene scarcely any of the propene reacted to form liquid hydrocarbons when contacted with concentrated sulfuric acid.

The amount of heptenes formed from the reaction of isobutene with propene varied from 8 to 35% (based on the liquid hydrocarbons produced) and was dependent on the concentration of the acid, temperature, and mode of addition of the olefins. The reaction of isopentenes with propene yielded hydrocarbons of which 16% were octenes and 17% tridecenes.

The combined lower boiling fractions of a number of isobutene-propene experiments were hydrogenated and then distilled through a 100-plate bubble cap still.³ Fractions amounting to 45% of the heptanes present were identified by physical properties and Raman spectra analysis as 2,2-dimethylpentane (A) and 5% as 2,2,3-trimethylbutane (B); another fraction (15% of the

heptanes) consisted of 2,3-dimethylpentane (C). (A) and (B) possess the carbon skeletons expected of primary polymers



but (C) probably results from a rearrangement of the 2,2-dimethylpentenes and/or 2,2,3-trimethylbutene under the influence of the sulfuric acid. Similar carbon skeleton isomerizations in the presence of acid catalysts have been observed by others.⁴

Several experiments were made in which the propene-isoolefin mixture was treated with isopropyl esters prepared by combining one mole of propene with one mole of 96% sulfuric acid. The proportion of propene which reacted with isoolefins was greater than in the case when sulfuric acid alone was used as a catalyst.

Experimental

Apparatus and Procedure.—The apparatus used for reactions at ordinary pressure was essentially the same as that described for previous experiments.¹ When higher temperatures and pressures were employed, a stainless steel stirring autoclave equipped with a copper liner was used. The sulfuric acid or its esters was placed in the reaction flask or in the autoclave and the olefin mixture passed into the rapidly stirred catalysts through an inlet tube. During the addition of the olefins the temperature was controlled by surrounding the reaction flask or chamber by an ice-bath or water-bath. The time required for the addition of the hydrocarbons varied from two to seven hours.

After being allowed to stand overnight at room temperature the two layers of the reaction product were separated.

(1) Ipatieff and Pines, *J. Org. Chem.*, **1**, 464 (1936).
 (2) Ormaudy and Craven, *J. Inst. Petr. Tech.*, **13**, 844 (1927), and *J. Soc. Chem. Ind.*, **47**, 317T (1928), found that propene underwent polymerization when passed slowly into 98% sulfuric acid.
 (3) Briun and Faulconer, *Ind. Eng. Chem., Anal. Ed.*, **9**, 192 (1937).

(4) (a) Laughlin, Nash and Whitmore, *THIS JOURNAL*, **56**, 1393 (1934); (b) Cramer and Glasebrook, *ibid.*, **61**, 230 (1939); (c) Drake, Kline and Rose, *ibid.*, **56**, 2076 (1934); (d) cf. review by Wachter, *Ind. Eng. Chem.*, **30**, 826 (1938).

TABLE I

Expt.	Temp., °C.	Reactants, g.			Reaction products, g.			Propene reacting to form HC, g.	Wt. % of liquid hydrocarbon product
		Catalyst	C ₃ H ₆	<i>i</i> -C ₄ H ₈	Acid layer	Hydrocarbon layer	Unreacted C ₃ H ₆		
1 ^a	0-20	273 ^b	369	442	384	624	36	122	8.2% C ₇ range
2 ^c	-18	388 ^d	295	310	383	509	70	132	14.2% C ₇ range
3	65-70 ^f	150 ^e	99	126	234	97	66		29.5% C ₇ range
4	100-110 ^g	150 ^e	99	126			14		35% C ₇ range
5 ^a	0-17	273 ^b	375	573 ^h	396	711	64	53	16% C ₈ range 17% C ₁₃ range

^a Total of three experiments. ^b 96% sulfuric acid. ^c Total of two experiments. ^d Monoisopropyl sulfate used; it was prepared by the addition of 2.74 moles of propene to 2.67 moles of 96% sulfuric acid. ^e 64% sulfuric acid. ^f Maximum pressure 191 lb./sq. in. ^g Maximum pressure 180 lb./sq. in. ^h Isopentenes used.

The hydrocarbon layer was steam-distilled from over alkali, dried, and distilled from over sodium. The sulfuric acid layer was decomposed with water, rendered alkaline with sodium hydroxide, and subjected to steam distillation. The distillate so obtained was saturated with potassium carbonate to complete the separation of the alcohols. The latter were dried and distilled.

Material non-volatile with steam was not analyzed; the nature and constitution of these high boiling fractions have been discussed in an earlier work.¹ The experimental conditions are given in Table I.

Isobutene-Propene Mixed Polymerization

Hydrocarbon Layer.—From the hydrocarbon product of the mixed polymerization of isobutene and propene there was obtained material boiling 75.2 to 78.6°; d_{20}^{20} , 0.689. *Anal.* Calcd. for C₇H₁₄: C, 85.62; H, 14.38; mol. wt., 98. Found: C, 85.60; H, 14.45; mol. wt., 97.

The presence of a *t*-butyl group in the heptene was shown by the method of depolyalkylation.^{5a} Fifteen cc. of the heptenes was dissolved in 19 g. of *t*-butylbenzene and the mixture was shaken with 10 cc. of 96% sulfuric acid at 0°. The hydrocarbon was then separated from the sulfuric acid, washed with alkali and water, and distilled. The fraction boiling 238-250° contained crystals of *p*-di-*t*-butylbenzene.

The combined lower boiling fractions of runs 1 and 2 were hydrogenated at 60° in the presence of nickel catalyst^{5b} and hydrogen, 100 kg./cm.² initial pressure. From the resulting paraffins the following fractions were separated by distillation through a 100-plate⁸ column.

Fraction	Cc.	B. p., °C. 750 mm.	n_{20}^{20}	d_{20}^{20}
1-3	29	69-77		
4	63	77-78	1.3838	0.6764
5	61	78-78.8	1.3830	.6738
6-10	59	78.8-88		
11	41	88-90.4	1.3928	.6960

Literature Data

2,2-Dimethylpentane ⁶	78.9 (760)	1.38233	0.6737
2,2,3-Trimethylbutane ⁶	80.9 (760)	1.38940	.6900 ⁷
2,3-Dimethylpentane ⁶	89.7 (760)	1.39201	.6952

(5) (a) Ipatieff and Pines, *THIS JOURNAL*, **58**, 1056 (1936); (b) Ipatieff and Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

(6) Edgar and Calingaert, *THIS JOURNAL*, **51**, 1540 (1929); Edgar, Calingaert and Marker, *ibid.*, **51**, 1483 (1929).

(7) Levene and Marker, *J. Biol. Chem.*, **91**, 77 (1931).

Raman Spectrum Analysis.⁸—Fractions 4 and 5 consisted of 90-95% 2,2-dimethylpentane, and 5-10% of 2,2,3-trimethylbutane. Fraction 11 consisted solely of 2,3-dimethylpentane.

Sulfuric Acid Layer.—The alcohols obtained from the sulfuric acid layer by the method described above were fractionated in a precision still. The following fractions were separated: (1) 79.4-80.0°, 78%, n_{20}^{20} 1.3782; (2) 80-84°, 17.5%, n_{20}^{20} 1.3785.

In order to determine whether *t*-butyl or isopropyl alcohol was produced, the entire product was dehydrated over alumina at 300°. By distillation on a low temperature Podbielniak distilling apparatus and by sulfuric acid absorption it was determined that the olefins formed consisted of pure propene.

Isopentene-Propene Mixed Polymerization

Hydrocarbon Layer.—Sixteen per cent. of the hydrocarbons consisted of octenes, b. p. 96-125°. The fraction boiling 100-116°, n_{20}^{20} 1.4174-1.4203, was hydrogenated at 100° (initial hydrogen pressure of 100 kg./sq. cm.) in the presence of a nickel catalyst. The hydrogenated product distilled between 112 and 116°; n_{20}^{20} 1.4033-1.4042; d_{20}^{20} 0.7168. *Anal.* Calcd. for C₈H₁₆: C, 84.10; H, 15.90; mol. wt., 114. Found: C, 83.95; H, 16.00; mol. wt., 113.

Sulfuric Acid Layer.—From the acid layer there was isolated an alcohol identified as isopropyl alcohol, b. p. 79-82°, n_{20}^{20} 1.3779-1.3782; 3,5-dinitrobenzoate, m. p. 121.5-122.¹⁰

Summary

Sulfuric acid catalyzed the reaction between propene-isobutene and propene-isopentenes to yield among other products heptenes and octenes, respectively. The hydrogenated heptenes contained 2,2-dimethylpentane, 2,3-dimethylpentane and some 2,2,3-trimethylbutane. These heptanes were identified by physical constants and Raman spectra analysis.

Propene alone under similar conditions does not undergo polymerization.

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(8) Raman spectra analyses by Dr. E. J. Rosenbaum, University of Chicago.

(9) Ipatieff, *Ber.*, **36**, 2011 (1903); Pines, *THIS JOURNAL*, **55**, 3892 (1933).

(10) Malone and Reid, *ibid.*, **51**, 3424 (1929).