

intensity; at least one is assignable to 1,2,3,4-tetrasubstituted benzene).

Attempts to prepare 1,6-dihydropyrene (III). VIII was found to be somewhat soluble in glacial acetic acid, so recrystallization from this solvent was attempted. After warming to get the material in solution, none would come out. Finally the solvent was removed by freeze drying, leaving a residue, m.p. 112–123°, which was soluble in benzene and ethanol. Chromatography of this material on alumina, using benzene as the eluent, gave a fast-moving band (characteristic of hydrocarbons) red in color. The material was recrystallized five times from petroleum ether (b.p. 60–68°)-hexane, m.p. 146–147°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. For $C_{16}H_{10}$: C, 95.19; H, 4.81. Found: C, 94.56; H, 5.40.

The ultraviolet spectrum (1.382 mg./l. in absolute ethanol) showed the material to be identical to pyrene. It was calculated that there was 89% pyrene in the sample.

The infrared spectrum (10% solution in carbon disulfide) also was very like that of pure pyrene.

Chromatography of this material on alumina was begun in an attempt to identify the colored material by separation of the hydrocarbon components. Elution with petroleum ether (b.p. 60–68°)-hexane²² was used. The pyrene fractions came off first as a white solid, m.p. 146–148°. (Pyrene when purified has a melting point of 150°.) A pale yellow band followed, but the amount of material recovered was not great enough to allow any physical measurements except a qualitative ultraviolet spectrum in ethanol solution. The spectrum again was that of pyrene so it is probable that autoxidation had occurred.

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(22) E. M. Charlet, K. P. Lanneau, and F. B. Johnson, *Anal. Chem.*, **26**, 861 (1954).

[CONTRIBUTION FROM POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & Co., INC.]

Synthesis of α -Hydroxyisobutyric Acid from Isobutylene

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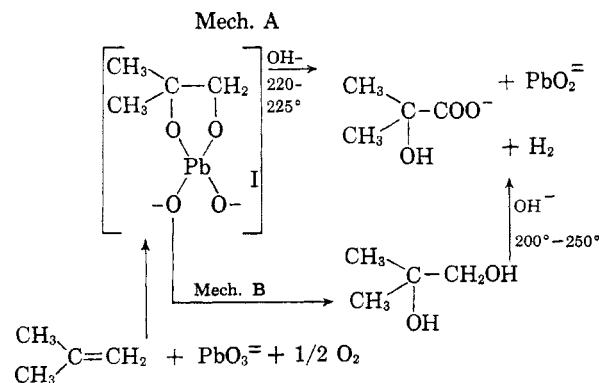
Isobutylene is oxidized with air in the presence of sodium plumbate/sodium hydroxide catalyst to α -hydroxyisobutyric acid. α -Hydroxyisobutyric acid is also obtained in good yields from isobutylene glycol and sodium hydroxide at 200–250°.

The air oxidation of isobutylene under a variety of conditions has been reported to give such products as methacrolein¹ and isobutylene glycol,² as well as compounds with fewer than four C-atoms.

We have found that sodium plumbate-sodium hydroxide mixtures are unique catalysts for the direct oxidation of isobutylene to α -hydroxyisobutyric acid (obtained as the sodium salt). The optimum conditions determined in this work employed a benzene solution of isobutylene, air at 1000 p.s.i. and temperatures of 200–250°. The yield varied markedly with the proportions of the reaction components and the preparation of the catalyst. Higher air pressures caused further oxidations; oxalic acid was detected under these conditions, probably resulting from oxidation of the benzene. Lower air pressures gave oily acids of low α -hydroxyisobutyric acid content. Satisfactory results were obtained only with the ratio of sodium plumbate-sodium hydroxide in the ranges 1:7 to 1:10.

The mechanism of the oxidation step of this reaction probably parallels that for permanganate oxidations. Wiberg³ has recently offered evidence for an intermediate cyclic permanganate ester. In analogy we may write a cyclic plumbate ester (I), the formation of which requires 0.5 mole of oxygen. This accounts for the observation that no re-

action takes place in the absence of oxygen even when molar amounts of sodium plumbate were used. The dehydrogenation step of this reaction may follow either of two mechanisms. The cyclic plumbate ester (I) may be dehydrogenated directly to α -hydroxyisobutyrate (Mech. A). Alternately, the plumbate ester (I) may be decomposed by direct alkaline cleavage to isobutylene glycol which is then dehydrogenated. Primary alcohols are known to be dehydrogenated to acids by heating with anhydrous alkali.⁴ We have been able to demonstrate that isobutylene glycol is dehydrogenated to α -hydroxyisobutyrate when heated with alkali to 250°.



(1) A. Clark and R. S. Shutt, U. S. Patent 2,383,711 (1945).

(2) C. E. Schweitzer, U. S. Patent 2,644,837 (1953).

(3) K. B. Wiberg, Abstracts of papers, page 60-P, 132nd American Chemical Society meeting, New York, N.Y., September 1957.

Although α -hydroxyisobutyric acid is the major product in this oxidation, it is not the only com-

(4) J. Dumas and J. S. Stas, *Ann. Chim. Phys.* (2), **83**, 113, *Ann.*, **35**, 129 (1840).

pound obtained. Formic acid is always found as a byproduct.

The intermediate plumbate ester (I) can, of course, react in other ways. Work-up of the neutral benzene-soluble products by distillation gave oily fractions and a solid, m.p. 63–64° (empirical formula $C_8H_{18}O_3$), the former showing both hydroxyl and carbonyl bands in the infrared, the latter only hydroxyl.

EXPERIMENTAL⁵

Preparation of sodium plumbate "catalyst." Sodium hydroxide pellets (80 g.) were fused in a nickel crucible. Lead oxide (44.6 g.) was added in portions while stirring with a spatula. If the temperature greatly exceeds the melting point, lumps form and the product is of inferior quality. Sodium peroxide (16 g.) was then added in small portions; the heat generated was usually enough to keep the mixture molten without further heating. After the addition, the crust on the edge of the crucible was melted with a burner. The temperature was then increased slowly with continuous stirring until a sudden increase in viscosity was observed. Stirring was continued until it was no longer possible. Caution should be exercised at higher lead oxide-sodium hydroxide ratios because the reaction is exothermic and can go to completion vigorously. Cold sodium plumbate-sodium hydroxide has a greenish yellow to tan color depending upon the concentration of the sodium plumbate in the sodium hydroxide. It is very hard and powdered with difficulty.

Oxidation of isobutylene. A 330-ml. stainless steel shaker tube was charged with 40 ml. of reagent benzene and 12 g. of finely powdered sodium plumbate-sodium hydroxide (1:10),⁶ closed and cooled to Dry Ice temperature; 22 g. of isobutylene was weighed in and 1000 p.s.i. air pressure was added at room temperature. The tube was shaken for 3 hr. at 200°. (The pressure at reaction temperature was 1700 p.s.i.) The contents of the shaker tube were then discharged at room temperature. The benzene slurry was filtered through a sintered funnel and the solid cake was washed with benzene. The golden yellow benzene solution contained the neutral compounds.

The solid residue, dissolved in 100 ml. of water, was passed through a folded filter to remove lead salts (no α -hydroxyisobutyric acid was retained by the lead salts). The aqueous filtrate was acidified with 10% sulfuric acid and extracted overnight in a continuous liquid-liquid extractor. The dried (magnesium sulfate) extract was evaporated, the last of the ether being driven off by heating at 60–70° for 30 min. The crude acid (4.0 g.) was freed from formic acid by evacuating at 30° (40 mm.) for 30 min. The α -hydroxyisobutyric acid crystallized completely; yield 2.9 g. (7% based on isobutylene charged). Several test runs show that only 4–5 g. of isobutylene actually reacted. The rest was recovered unchanged. The corrected yields in the oxidation of isobutylene to α -hydroxyisobutyric acid is thus 30–40%.

(5) Melting points are uncorrected. Infrared spectra were determined on a Perkin-Elmer double beam spectrophotometer, Model 21. The analysis was performed in the analytical laboratory of the Polychemical Department.

(6) More sodium plumbate sodium hydroxide (1:10) or higher sodium plumbate concentration gave more formic acid, less plumbate, only oily acids.

Part of the crude α -hydroxyisobutyric acid was distilled *in vacuo* (b.p. 106–109°/2 mm.) and recrystallized from benzene. The m.p., 78–79°, was not depressed by an authentic sample of α -hydroxyisobutyric acid. The infrared spectra of both samples were superimposable.

Partition chromatography was applied to another part of this crude acid for additional identification and to obtain a quantitative determination of α -hydroxyisobutyric acid content. Two small peaks (not identical with either isobutyric acid or methacrylic acid) appeared before α -hydroxyisobutyric acid (89%) and a small amount remained on top of the chromatographic column.

Partition chromatography of the acids. The procedure was essentially that of Marvel and Rands⁷ for aliphatic acids.

The stationary phase was 20 g. of Mallinckrodt 100-mesh silicic acid impregnated with 17 ml. of 0.5N sulfuric acid. About 0.1 g. of the above crude α -hydroxyisobutyric acid was placed on the column and eluted with successive portions of chloroform, 5% *n*-butyl alcohol, and finally 10% *n*-butyl alcohol in chloroform. Each solvent mixture was saturated with water before use. Successive 10-ml. fractions were titrated with 0.02N sodium hydroxide solution to a cresol red end point.⁸

Some peak effluent volumes of acids are given which were not reported in the literature.

Isobutyric acid	70 ml.
Methacrylic acid	100 ml.
α -Hydroxyisobutyric acid	290 ml.

α -Hydroxyisobutyric acid from isobutylene glycol. Isobutylene glycol (45 g.) and sodium hydroxide (30 g.) were heated in a shaker tube under nitrogen at 250° for 3 hr. The reaction mixture was dissolved in 200 ml. of water and extracted with ether for 8 hr.; 1.8 g. of starting material was recovered. Acidification with 10% sulfuric acid and ether extraction overnight gave 37.7 g. of crude acids which solidified upon standing. One recrystallization from benzene gave 23.9 g. (50%) of α -hydroxyisobutyric acid, m.p. 76–78°. Another recrystallization from benzene raised the m.p. to 78–79°. The melting point was not depressed on mixture with an authentic sample and the infrared spectra were identical.

Neutral compounds. The benzene solutions of 25 runs were collected; the benzene was removed and the residue (15 g.) distilled at reduced pressure (2 mm.). Cuts from 25–57° showed infrared bands at 2.85 μ , 5.85 μ , and 6.00 μ . The fraction, b.p. 57–60° crystallized and was triturated with cold pentane giving 1.1 g., m.p. 60–63°; two crystallizations from pentane gave colorless needles, m.p. 63–64°.

Anal. Calcd. for $C_8H_{18}O_3$: C, 59.23; H, 11.18. Found: C, 59.6; H, 11.2.

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(7) C. S. Marvel and R. D. Rands, *J. Am. Chem. Soc.*, **72**, 2642 (1950). The chromatographic behavior of isobutyric acid, α -hydroxyisobutyric acid, and methacrylic acid, all possible oxidation products of the isobutylene oxidation, were not described in his paper. It was, therefore, determined first on an artificial mixture of known acids, before the unknown mixtures were analyzed.

(8) Electrometric end point determination was less satisfactory. Control experiments showed that methacrylic acid and isobutyric acid could be readily separated from α -hydroxyisobutyric acid. The separation of methacrylic acid from isobutyric acid is poor.