

[CONTRIBUTION FROM THE EMERYVILLE RESEARCH CENTER OF SHELL DEVELOPMENT CO.]

Reactions of Hydrogen Peroxide. I. A Novel Use of Selenium Dioxide as Catalyst for Oxidation of Acrolein to Acrylic Acid

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By a novel use of selenium dioxide as catalyst, hydrogen peroxide has been used to oxidize acrolein and methacrolein to monomeric acrylic and methacrylic acids. Systems with low water content gave highest yields of monomeric acids. Such solutions from 35% hydrogen peroxide in *tert*-amyl alcohol were produced by azeotropic removal of water. In all cases the peroxide content was kept below 15% by weight.

With the availability of acrolein and hydrogen peroxide as articles of commerce, means have been sought for combining them in the preparation of acrylic acid. In the absence of catalyst and in aqueous solution these materials showed little tendency to react. With standard peracid-forming catalysts such as formic, acetic, and tungstic, the aldehyde group was oxidized but polymerization and other reactions occurred so that only crude polymeric acids were obtained. After some searching, selenium dioxide was found to catalyze the formation of monomeric acrylic and methacrylic acids from acrolein and methacrolein.

Catalyst. Although selenium dioxide has been used as a reactant and catalyst in many other reactions, this is the first time it has been used in just this way. Oxidations of methylene groups adjacent to carbonyl groups with stoichiometric quantities of selenium dioxide to give α -diketones or ketoaldehydes are well known. Even certain methyl groups adjacent to aromatic rings can be oxidized to aldehydes, but the reaction apparently stops here. Thus these reactions leading to aldehydes or ketones are different from the present one producing acids. In another obviously different case¹ selenium dioxide with hydrogen peroxide has been used for the hydroxylation of cyclopentene and cyclopentadiene. The catalyst in this case is probably perselenic acid.

Reaction conditions. Conditions and results in the preparation of acrylic and methacrylic acids are closely analogous. The preparation of acrylic acid will be reviewed first and significant differences with methacrylic acid will then be given.

In the present oxidation of acrolein, tertiary alcohols containing only small amounts of water were used as solvents. At the optimum temperature, 40°, the reaction time was 3 hr. At the end of the reaction the catalyst precipitated as red elemental selenium. Anhydrous acrylic acid was obtained by distillation without further treatment. After the peroxide had been consumed and precipitation of selenium had started the temperature could be raised as high as 100° without causing polymerization.

Apparently selenium inhibits the polymerization of acrylic acid.

Selenium dioxide is so far the only practical catalyst found for this reaction. At the concentrations used (5.0 g. SeO_2 per mole of H_2O_2) it was completely soluble in the reaction mixture. At concentrations of 1 g. of SeO_2 per mole of peroxide a much slower reaction occurred and poor yields of acrylic acid were obtained. Two other catalysts, phosphotungstic acid and selenotungstic acid, gave low conversions to distilled acrylic acid.

Two schemes were used for recovery of selenium. With excess acrolein the elemental selenium formed at the end of the reaction was collected on a filter. With a slight excess of peroxide the selenic acid was removed with a weakly basic, ion-exchange resin (Amberlite IR4B). Sodium selenate was recovered by leaching the resin with 10% sodium hydroxide.

Reaction intermediates. Although not established, the course of the present reaction is thought to involve oxidation of selenous to selenic acid with hydrogen peroxide. Acrolein then reacts with the selenic acid to give acrylic and selenous acids. As long as acrolein is present to react with selenic acid probably little if any perselenic acid is formed.

To evaluate the possibility that initial reaction is between the dioxide and acrolein, stoichiometric quantities of the two materials were allowed to react. The major product was not identified but no indication of acrylic acid could be found.

Solvent. The reaction was usually carried out with *tert*-butyl or *tert*-amyl alcohol as solvent. A simple expedient to obtain essentially anhydrous solutions of hydrogen peroxide without handling the hazardous 90% material was to remove water azeotropically from solutions of more dilute peroxide in the desired alcohol. To minimize possibilities for detonable mixtures, the concentration of peroxide in alcohol was not allowed to exceed about 15%. Little or no esterification of acidic products occurred during the reaction with the tertiary alcohols as solvents. With the primary and secondary alcohols as solvents, formation of acid is accompanied by esterification. However, combined conversions (90–100%) to acid and ester (as indicated by titration) were the same as to acid alone with the tertiary alcohols. Oxidation in methyl, ethyl, allyl, and *n*-

(1) Stoll, Lindenmann, and Jucker, *Helv. Chim. Acta*, **36**, 268 (1953).

butyl alcohols and in ethylene glycol gave some 15–40% of the corresponding acrylates. Unfortunately, the only quantitative study used for acrylic acid and esters in the flashed distillates was titration with base and saponification. In one case acrylic acid was isolated (but not quantitatively) by fractional distillation of the flashed distillate and identified by melting point and mixed melting of its crystalline derivative, β -anilinopropionanilide.

With increasing concentration of water an increased conversion to polymeric acid takes place. Thus with anhydrous or 90% hydrogen peroxide about a 5% conversion to polymer occurs; with 35% peroxide the conversion to polymer is 10% or higher. With water alone as the solvent, only polymer was obtained. In all these cases, the acidity as indicated by titration was 0.95–1.00 equivalent based on acrolein charged, only the conversion to polymer varied markedly. It seems probable that with increasing amounts of water an increase in ionization of the selenic and selenous acids takes place and this increased acidity causes polymerization of the acrolein and/or acrylic acid with a consequent decrease in conversion and yield of monomeric acrylic acid. This view may be supported by the observation that addition of 0.3% sulfuric acid to a standard reaction mixture increases polymer formation so that about equal amounts of monomeric acid (47.9%) and polymer (48.5%) were formed.

Methacrolein was oxidized to methacrylic acid in 93% yield under essentially the same conditions used with acrolein. Here a reaction temperature of 60–70° is possible without reducing the yield due to polymer formation. At this temperature a reaction time of about 1.5 hr. is sufficient. A few non-hydroxylic solvents were also investigated. In dioxane essentially the same conversion to monomeric methacrylic acid was obtained as in alcohol. The use of benzene and acetone as solvents lowered the conversions from 90–95% to 85% while in acetic acid the conversion was only 54%.

EXPERIMENTAL

Azeotropic removal of water from H₂O₂ in tert-amyl alcohol. A mixture of 198 g. (2.0 moles) of 34.7% H₂O₂ and 1000 g. of tert-amyl alcohol was distilled under a phase-separating stillhead at a pressure of 50 mm. The lower water phase was drawn off as it collected in the stillhead and the upper alcohol phase returned to the kettle. A maximum kettle temperature of 50° was reached. After about 110 cc. of water had been removed, reflux was discontinued and about 400–500 cc. of alcohol was collected. Titration of the residue in the kettle showed 12.09% H₂O₂ and 0.85% H₂O. This represents about a 95% recovery of H₂O₂.

Oxidation of acrolein to acrylic acid. In a four-neck flask having a stirrer, dropping funnel, thermometer, and condenser were placed 103 g. of tert-amyl alcohol, 5.0 g. of selenium dioxide, and 56 g. (1.0 mole) of acrolein. A solution of 281 g. (1.0 mole) of 12.09% H₂O₂ in tert-amyl alcohol was then added dropwise in 30 min. with cooling at 40°. Three hours from the start a titration indicated 0.925 equivalents of acid other than selenous or selenic had been produced.

After standing overnight (about 20 hr. from start), another titration indicated the same amount of acid. The product was distilled rapidly from a Claisen flask directly into a large cold trap cooled in a dry ice-acetone mixture. A pressure of 100 mm. was used and the kettle was warmed with a hot water bath. Near the end the pressure was reduced to 1 mm. The distillate weighed 457 g. and contained 0.900 equivalents of acid by titration. The residue weighed 9.5 g. Analysis of the distillate showed 0.07% acrolein. The 0.900 equivalent of acid represents a 90.0% conversion of H₂O₂ to distilled acid and a 90.5% yield based on acrolein.

In a similar experiment, except that tert-butyl alcohol was used as solvent, the flashed distillate contained 0.696 equivalents of acid. This distillate was redistilled from a Claisen flask. The fraction boiling 53–87° (100 mm.), 98.1 g. was distilled through a 1 × 25 cm. glass-helices packed column after addition of a small amount of hydroquinone. When the head temperature reached 50° (100 mm.), the pressure was reduced to 10 mm. and the acrylic acid which flashed weighed 22.6 g. This represents a 45% recovery of the acrylic acid indicated to be present by titration. This lack of material balance is probably due to acrylic acid which distilled with the alcohol and to some polymer formation during distillation.

Anal. Calcd. for C₂H₄O₂: Neut. equiv., 72. Found: Neut. equiv. 75.

Heating the above product with aniline gave β -anilino-propionanilide which melted at 91–92° after recrystallization from aqueous ethanol.

Anal. Calcd. for C₁₅H₁₆N₂O: C, 75.0; H, 6.7; N, 11.7. Found: C, 74.9; H, 6.8; N, 11.7.

β -Anilinopropionanilide prepared similarly from an authentic sample of acrylic acid melted at 93–93.5°. A mixture of the two materials melted at 93–93.5°.

Oxidation of methacrolein to methacrylic acid. A solution of 5 g. of selenium dioxide in 350 g. of tert-butyl alcohol was combined with 105 g. (1.5 moles) of methacrolein and stirred while 35 g. (1.0 mole) of 90% hydrogen peroxide was added dropwise in 17 min. Cooling was applied to keep the temperature at 60°. After 1.5 hr. a titration indicated 0.95 equivalents of acid had been generated. The product was stripped of all volatile material by warming in a water bath at 55–60° (80 mm.) and finally at 75° (1 mm.). This left 11 g. of red residue and took overhead 484 g. of distillate containing 0.937 equivalents of acid. A 434 g. portion of the distillate was redistilled through a small helices-packed column having 4 copper wires² running through the packing for the length of the column to act as a polymerization inhibitor. A piece of copper wire was also suspended in the stillhead. After the alcohol and a small intermediate cut of 4.5 g., methacrylic acid, 43.5 g., was collected at 69–71°, n_D^{20} 1.4298–1.4309. This center cut represents a 74% recovery of methacrylic acid indicated by titration to be present.

Anal. Calcd. for C₄H₆O₂: C, 55.80; H, 7.03; Br. No. 186 g. Br/100 g.; Neut. equiv. 86. Found: C, 55.81; H, 7.04; Br. No. 185 g. Br/100 g.; Neut. equiv. 87.

Heating the above product with aniline gave β -anilinoisobutyranilide which melted at 119–120°.

Anal. Calcd. for C₁₅H₁₈N₂O: C, 75.6; H, 7.1; N, 11.0. Found: C, 75.6; H, 7.6; N, 10.9. A mixture of the above derivative with β -anilinoisobutyranilide (m.p. 119–120°) prepared similarly from an authentic sample of methacrylic acid melted at 119–120°.

n-Butyl acrylate from oxidation of acrolein in n-butanol. A solution of 56 g. (1.0 mole) of acrolein and 5.0 g. of selenium dioxide in 350 g. of n-butanol was kept at 40° while 38 g. (1.0 mole) of 90% hydrogen peroxide was added in 10 min. After about 5 hrs. the clear yellow solution began turning red with precipitated selenium. After standing overnight at

(2) In his book "Vinyl and Related Polymer," John Wiley and Sons, Inc., New York 1952, p. 298, C. E. Schildknecht states that traces of copper salts of acrylic acid are effective inhibitors of polymerization of acrylic acid.

room temperature, the opaque red suspension was titrated. There was 0.791 equivalent of acid and 0.239 equivalent of ester. The product was flashed under vacuum using a hot water bath. There was taken overhead 70 g. of distillate leaving 15 g. of somewhat viscous liquid residue. Titration of the distillate showed 0.701 equivalent of acid and 0.194 equivalent of ester and 2.1 g. of acrolein.

Oxidation of acrolein with selenium dioxide. To a suspension of 55.5 g. (0.5 mole) of selenium dioxide in 350 g. of *tert*-butyl alcohol was added 56 g. (1.0 mole) of acrolein all at once. The reaction was warmed and maintained at 40°. The color changed from white to red in about 0.5 hr. After standing overnight at room temperature, filtration of the mixture gave 40.7 g. of selenium. The filtrate was distilled at 50° (25

mm.). The colorless distillate contained no acid as shown by titration.

Formic acid catalyzed oxidation of acrolein. A slow consumption of peroxide took place when 1.15 moles of acrolein, 1.15 moles of hydrogen peroxide, and 1.0 mole of formic acid in 500 cc. of water was left at room temperature. After 8 days 77.5% of the H₂O₂ was gone and 0.84 mole of acid had been generated. Evaporation of the solvents at less than 50° left 84 g. of a very viscous water-soluble polymer with analysis indicative of a crude poly(acrylic acid).

Anal. Calcd. for C₃H₄O₂: C, 50.00; H, 5.59; Neut. equiv. 72. Found: C, 49.25; H, 6.31; Neut. equiv. 109.

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Studies in Organosilicon Chemistry. XXXIV. The Reaction of Trimethylsilylmethyl Metallic Compounds with Trichlorosilane

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Trichlorosilane and trimethylsilylmethylmagnesium bromide react in 2.5:1 molar ratio to form trimethylsilylmethyl-dichlorosilane, in 0.33:1 ratio to give bis(trimethylsilylmethyl)chlorosilane and in 0.30:1 ratio giving an 18.6% yield of tris(trimethylsilylmethyl)silane. Trichlorosilane and trimethylsilylmethyl lithium react in 0.22:1 molar ratio forming tris(trimethylsilylmethyl)silane in 71% yield. The product undergoes bromination giving tris(trimethylsilylmethyl)bromosilane which can be hydrolyzed by aqueous ammonium hydroxide in acetone to form tris(trimethylsilylmethyl)silanol. Trimethylsilylmethyl dichlorosilane undergoes hydrolysis to poly(trimethylsilylmethyl)siloxanes. Infrared absorption curves are presented for tris(trimethylsilylmethyl)silane, tris(trimethylsilylmethyl)silanol and poly(trimethylsilylmethyl)siloxanes, I(fraction 1), II(fraction 2), and III(fraction 3).

The steric effect of highly-branched groups in aliphatic organosilicon compounds is manifested in the reactivity or non-reactivity of certain functional groups attached to the silicon.^{1,2,3,4,5} In line with some of this previously reported work, a series of compounds has been prepared and studied in which the trimethylsilylmethyl group has been substituted for one or more chlorines in trichlorosilane. Silanols containing large groups attached to silicon are quite stable toward condensation, in contrast with those with smaller groups.^{6,7}

Trimethylsilylmethylmagnesium bromide reacts with trichlorosilane in various proportions, to form the mono-, the di-, and the trisubstitution products. Tris(trimethylsilylmethyl)silane reacts with bromine to form tris(trimethylsilylmethyl)bromosilane and this compound undergoes hydrolysis to

form the corresponding silanol, isolable as such. (Trimethylsilylmethyl)dichlorosilane undergoes hydrolysis to give the trimeric and tetrameric forms of (trimethylsilylmethyl)siloxane. Trimethylsilylmethyl lithium reacts with trichlorosilane to form tris(trimethylsilylmethyl)silane.

TABLE I
TRIMETHYLSILYLMETHYLSILANES

	B.P. °C	Mm.	n_D^{25}	d_4^{25}
(CH ₃) ₃ SiCH ₂ SiHCl ₂	52.0-53.5	24		
	146-148			
[(CH ₃) ₃ SiCH ₂] ₂ SiHCl	79-80	5		
[(CH ₃) ₃ SiCH ₂] ₃ SiH	108 ^a	9 ^a	1.4495 ^a	0.8221 ^a
	103-107 ^b		8 ^b	1.4498 ^b
[(CH ₃) ₃ SiCH ₂] ₃ SiBr	110	1.8	1.4725	
[(CH ₃) ₃ SiCH ₂] ₃ SiOH	112-113	5.0	1.4540	0.8594

^a Through the Grignard reagent. ^b Through the organolithium compound.

Infrared absorption curves (Fig. 1) are presented for the first of the polymeric materials listed in Table II, as well as for tris(trimethylsilylmethyl)silane, and for tris(trimethylsilylmethyl)silanol. The scanning speed was one micron per minute, with a normal slit, and a sample cell of 0.025 mm. The reference was air at 24° with no solvent.

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