

Oxidation of Benzyl Alcohol and Benzaldehyde with Xenon Trioxide

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Benzyl alcohol is oxidized by xenon trioxide in acidic or neutral solution to benzaldehyde and benzoic acid. The course of the reaction was followed by gas chromatography. Thin-layer chromatography was used to identify the products of oxidation.

THE OXIDIZING properties of xenon trioxide in aqueous solution have been reported by Williamson and Koch (1) and by Appelman and Malm (2). In acid solution xenon trioxide was shown to be a very powerful oxidizing agent with the advantage that in the reduced form (xenon gas) it is relatively insoluble and does not contaminate the reaction mixture. However, only a few reports have appeared in the literature dealing with the application to the oxidation of organic compounds. Jaselskis and Vas (3) performed a series of qualitative studies on the oxidation of certain *vic*-diols with xenon trioxide. It was presumed that the reactivity of this oxidizing agent was similar to that of periodic acid. Xenon trioxide was found to react readily with ethylene glycol, 2,3-butanediol, and certain primary alcohols in neutral and basic solution. No reaction was noted in acidic solution. In a subsequent paper Jaselskis and Warriner (4) reported a quantitative method for the determination of primary and secondary aliphatic alcohols in aqueous solution. This study was limited to methanol, ethanol, and 2-propanol. It was applicable for both macro and semimicro quantities of alcohol. Jaselskis and Krueger (5) extended the procedure to include a series of mono- and dicarboxylic acids.

In the present paper the xenon trioxide oxidation of benzyl alcohol and benzaldehyde to benzoic acid is reported.

EXPERIMENTAL

Apparatus—A WCLID 1670 gas chromatograph¹ was employed for detection of the products of oxidation and for following the course of the reaction. It was equipped with dual hydrogen flame ionization detectors and stainless steel columns. The 6 ft. \times $\frac{1}{8}$ in. o.d. columns² were packed with 60–80 mesh flux calcined diatomaceous earth coated with 15% diethylene glycol succinate and 13% phosphoric acid.³ The columns were operated at the following temperatures: 140° for the determination of benzyl alcohol, 120° for benzaldehyde, and 195° for benzoic acid. The injection port was maintained at 200°. A Hamilton syringe (701-N) was employed for injection of samples. Hydrogen gas flow rate was maintained at 5 ml./min., air at 300 ml./min., and nitrogen gas at 50 ml./min.

For the thin-layer chromatography studies, 20 \times 5 cm. glass plates, a Desaga variable-gate spreader, and cylindrical development tank were used. A Mineralight ultraviolet lamp,⁴ short

wave UVS-12, was employed for visualization of colorless zones.

Solutions and Reagents—Benzyl alcohol solution was 0.05 *M* in concentration. For benzoic acid and benzaldehyde, saturated solutions in water were used. Xenon trioxide solution was 0.02 or 0.06 *M* and was prepared by diluting a concentrate (0.2 *M*) with water. The preparation of concentrated xenon oxide solutions is described by Appelman and Malm (2). Since solid xenon trioxide has a tendency to explode, solutions were stored in tightly stoppered flasks at all times. A saturated aqueous solution of potassium iodide was kept at hand to inactivate any spilled or unspent xenon trioxide solution.

Ammoniacal fuchsin reagent (6), 2,4-dinitrophenylhydrazine T.S. (7), and ferric chloride T.S. (6) were used for identification of benzaldehyde and benzoic acid.

Silica Gel HF₂₅₄ (Merck) and Silica Gel G according to Stahl were used for the preparation of the thin-layer chromatographic plates. All chemicals and solvents were reagent grade.

Procedure—*Gas Chromatography*—Exactly 250 μ l. of 0.05 *M* benzyl alcohol and 250 μ l. of 0.06 *M* xenon trioxide solution were transferred by micropipet to a 2 dr. clear glass screw-top vial. The vial was tightly capped and permitted to stand at room temperature. Corresponding reaction mixtures of benzaldehyde and benzoic acid were prepared in a similar manner. Four controls were prepared containing 250 μ l. of the following solutions: benzyl alcohol, benzaldehyde, benzoic acid, and xenon trioxide.

One microliter of each reaction mixture was injected into the gas chromatograph at zero time, after 5 min., and then every 15 min. for 9 hr. The retention times for the oxidation products were determined. The control solutions were injected into the chromatograph and retention times were calculated and used for identification of the oxidation products. The concentrations of the components were calculated by integration of the peak areas and comparison with those obtained from standard solutions of varying concentrations.

Thin-Layer Chromatography—Exactly 250 μ l. of 0.05 *M* benzyl alcohol and 500 μ l. of 0.02 *M* xenon trioxide solution were transferred by micropipet to a 2 dr. vial. A second reaction mixture was prepared using exactly 250 μ l. of 0.025 *M* benzaldehyde solution in place of the benzyl alcohol. The vials were tightly stoppered and permitted to stand at room temperature for 48 hr.

Adsorbent layers, 500 μ in thickness, were prepared by applying aqueous slurries (40 Gm. with 100 ml. water) of Silica Gel HF₂₅₄ or Silica Gel G onto glass plates. Air-drying overnight at room temperature provided adequate activation of the adsorbents. Sample solutions of the reaction mixtures and controls were each spotted portionwise in 5- μ l. quantities. Development of the plates was conducted in an ascending manner in tanks pre-

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¹ Purchased from Warner-Chilcott Laboratories, Instruments Division, Richmond, Calif.

² Prepared by Chemical Research Services, Inc., Addison, Ill.

³ Gas-Pack W.

⁴ Ultraviolet Products, Inc., San Gabriel, Calif.

TABLE I—RATE OF OXIDATION OF BENZYL ALCOHOL AND BENZALDEHYDE AND THE RATE OF FORMATION OF BENZOIC ACID BY VAPOR PHASE CHROMATOGRAPHY

Benzyl Alcohol ^a		Benzaldehyde ^b		Benzoic Acid ^c	
Time, min.	Concn., mm./ml.	Time, min.	Concn., mm./ml.	Time, min.	Concn., mm./ml.
0	0.0500	0	0.0250	180	0.0010
60	0.0400	90	0.0200	300	0.0015
165	0.0250	225	0.0150	480	0.0050
240	0.0200	285	0.0125	540	0.0050
360	0.0125	390	0.0100		

^a Column temperature, 140°; retention time, 65 sec.
^b Column temperature, 120°; retention time, 54 sec. ^c Column temperature, 195°; retention time, 40 sec.

viously equilibrated for 20 min. with the appropriate solvent mixture. Visualization of the plates was carried out either directly or by scanning with an ultraviolet lamp.

For the detection of benzoic acid, a plate layered with Silica Gel HF₂₅₄ was spotted with the reaction mixtures and a control solution of benzoic acid, developed 70 min. to a solvent front migration of 14.7 cm. with chloroform-cyclohexane-acetic acid (80:20:10), and visualized by ultraviolet light scanning.

For the detection of benzaldehyde, aliquots of the benzyl alcohol reaction mixture and a control solution of benzaldehyde were first treated with an excess of 2,4-dinitrophenylhydrazine T.S., before spotting on an adsorbent layer of Silica Gel G. A sample of the 2,4-dinitrophenylhydrazine T.S., as a control, was also spotted on the plate. The chromatogram was developed for 30 min. to a solvent front migration of 17.0 cm. with benzene-ethyl acetate (95:5), air-dried, and examined visually.

RESULTS AND DISCUSSION

In acidic or neutral solution benzyl alcohol is oxidized at room temperature, first to benzaldehyde, and then to benzoic acid. The course of the reaction was followed by vapor phase chromatography. The data are shown in Table I. The retention times for benzyl alcohol, benzaldehyde, and benzoic acid were 65, 54, and 40 sec. The half-time for the oxidation of benzyl alcohol to benzaldehyde was 165 min., and for benzaldehyde it was 285 min. The presence of benzaldehyde and benzoic acid in the reaction mixture was confirmed by comparison of the retention times with those of the control

solutions. In addition, the reaction mixture was augmented with samples of known benzaldehyde and benzoic acid. Single peaks were produced for each component and the area under the curve increased by the amount of the component added to the reaction mixture. The presence of benzaldehyde and benzoic acid in the reaction mixture was further confirmed by testing qualitatively with ammoniacal fuchsin and ferric chloride test solutions, respectively.

The reaction mixture was also studied by thin-layer chromatography of Silica Gel HF₂₅₄, a fluorescent adsorbent. Prior to development, the spotted zones at the origin appeared as dark areas against a brightly fluorescent background when viewed under ultraviolet light. After development of the chromatogram, dark zones were detected at an R_f of 0.65 for the reaction mixtures as well as for the known benzoic acid sample. This test confirmed the presence of benzoic acid in the reaction mixtures. The test proved unsatisfactory for the detection of benzaldehyde because of its loss by volatilization during the drying treatment of the chromatogram. Detection of benzaldehyde, however, was successful through the formation of the 2,4-dinitrophenylhydrazone derivative. The benzaldehyde in the reaction mixture and a known sample of benzaldehyde were converted to the hydrazone derivative which was detected as bright yellow zones on Silica Gel G with an R_f value of 0.75. A corresponding zone was absent for the reagent sample which served as a control. A yellow zone corresponding to 2,4-dinitrophenylhydrazine and having an R_f of 0.50 was apparent for the reaction mixture, the known benzaldehyde solution, and the reagent solution.

Under the conditions of this study the reaction appears to be quantitative. Further studies are now in progress involving the oxidation of other aromatic alcohols, certain organic sulfides, and a variety of amines.

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