Method for Identifying Isobutylene

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A method for the identification of isobutylene (2-methylpropene) is based on the catalyzed absorption of isobutylene in phenol and the formation of 4-*tert*-butylphenol. This reaction may also be applied to the identification of 2-methyl-1-butene and 2-methyl-2-butene by formation of 4-*tert*-pentylphenol.

IN WORK on the thermal decomposition products of Diels-Alder adducts of certain terpenes, it became necessary to establish the presence of small amounts of isobutylene (2-methylpropene). Isobutylene has been identified chemically by formation of the nitroso chloride (*3*), the nitrosate (*3*), the nitrosite (*6*), and the dibromide (*2*), but none of these methods is entirely satisfactory.

Isobutylene reacts with phenol in the presence of a catalyst to form the butyl ether which readily rearranges to form 4-*tert*-butylphenol, melting at 99° C. However, this reaction apparently has not been used for identifying isobutylene, although the high melting point and good yields reported (*4*) would seem to make the reaction a promising one. In the present work, this reaction was investigated as a means of identifying isobutylene and was found suitable. The reaction conditions are not critical and the apparatus required is simple. The method was also found suitable for the identification of the pentenes, 2-methyl-1-butene and 2-methyl-2-butene. All three olefins were successfully identified among the decomposition products of various terpene Diels-Alder adducts. Deliberate admixture of isobutylene with equal volumes of ethylene, propylene, or acetylene did not interfere with the formation and isolation of 4-*tert*-butylphenol. Admixture of isobutylene with an equal volume of butadiene decreased the yield somewhat but pure 4-*tert*-butylphenol was isolated without difficulty.

APPARATUS AND EXPERIMENTAL PROCEDURE

The reaction is carried out in a test tube (20 ml.) fitted with a side arm and one-hole rubber stopper carrying a glass tube drawn to a point and extending to within 1 or 2 mm. of the bottom (Figure 1). The tube is heated by a suitable bath. The isobutylene is displaced from the storage container by water added from a separatory funnel and may be dried by passage through a calcium chloride drying tube, if desired, before being passed into the reaction tube. Unabsorbed gas is collected over water in a graduate.

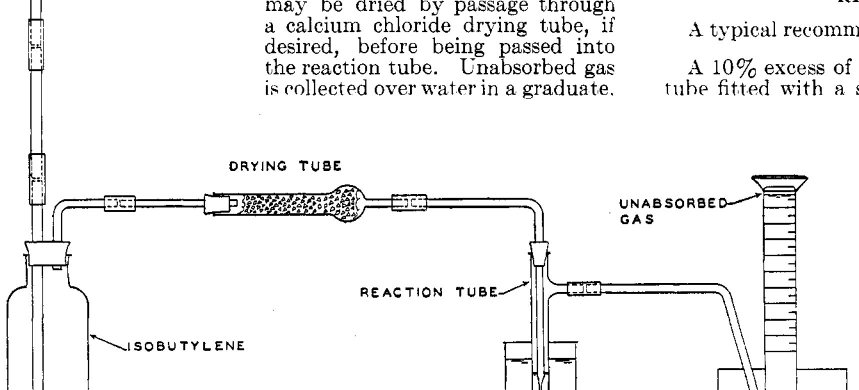

Figure 1. Apparatus for Absorption of Isobutylene

The isobutylene was prepared by refluxing 25 ml. of *tert*-butyl alcohol with 8 grams of hydrated oxalic acid (*1*). The gas was collected in 500-ml. storage bottles by displacement of water and stored until use. Three procedures were found to be satisfactory for absorbing the olefin in the phenol-catalyst mixture. In the first method, the gas is bubbled through the mixture by displacement of the gas in the storage bottle; water is added from a separatory funnel at such a rate as to result in substantially complete absorption, and unabsorbed gas is collected and measured. In the second, which can be used only if the isobutylene is fairly pure, the gas is passed into the closed reaction tube under a head of about 75 cm. (30 inches) of water after most of the air has first been removed by evacuation. In the third method, the side arm of the reaction tube is kept open until about 20 ml. of gas have passed through, the side arm is then closed off by means of a pinch clamp, and the isobutylene is absorbed as in method 2. If the absorption slows down, owing to an accumulation of unreacted gas, the side arm can again be opened to purge the tube of such gas.

A number of trials were made to observe the effect of variation in the quantity of phenol and the quantity and concentration of the catalyst; drying of the isobutylene; temperature of the reaction mixture during absorption; and additional heating. Additional excess phenol tended to increase the rate of absorption but did not increase the yield significantly. The presence of small amounts of moisture did not significantly affect the yield, and use of 96% sulfuric acid and isobutylene dried by passage over calcium chloride gave substantially the same yield as 75% sulfuric acid used with isobutylene which was not dried with calcium chloride after displacement by water. An increase in temperature during absorption tended to decrease the time required to complete absorption and gave somewhat higher yields (10% total yield at 60° C. compared to 15% at 80°); but additional heating at 125° or 140° significantly increased yield. Thus, 1 hour of additional heating at 125° after absorption was completed raised the yield to 75%. Neither heating for more than 1 hour at 125° nor heating for 1 hour at 140° further increased yield. Use of other catalysts, such as oxalic-boric acid or aluminum chloride, did not give as good results as did sulfuric acid.

RECOMMENDED PROCEDURE

A typical recommended procedure is given below:

A 10% excess of phenol (2.17 grams) is placed in a 20-ml. test tube fitted with a side arm and 0.1 ml. of concentrated sulfuric acid is added. The test tube is then shaken by hand and placed in an oil bath maintained at 90° C. The side arm is connected by a short length of glass tubing to an inverted graduate filled with water to measure the volume of any unabsorbed gas. The mouth of the test tube is fitted with a one-hole rubber stopper carrying a glass gas inlet tube drawn to a point and extended to within 1 or 2 mm. of the bottom. A bottle containing 500 ml. of isobutylene is fitted with a two-hole rubber stopper carrying a 500-ml. separatory funnel and an outlet tube, and the outlet tube is connected to the gas inlet tube of the reactor. The isobutylene is displaced by adding water from the separatory funnel at a rate sufficient to cause bubbling in the absorption tube but substantially no escape of unabsorbed isobutylene into the inverted graduate. This requires 20 to 30 minutes and about 20 ml. of unabsorbed gas (chiefly air displaced from the system) are collected in the graduate. The reaction tube is then disconnected, the temperature of the bath is raised to 125°, and heating is continued for an additional hour. The hot reaction mixture is then poured into 40 ml. of water and shaken vigorously by hand to remove the acid and any unreacted phenol. Crystallization occurs soon after shaking is begun. The colorless needles so obtained are filtered off by suction, washed with 5 to 10 ml. of water, and dried to constant weight in a vacuum desiccator.

Using this procedure, 2.45 grams (76% yield) of product melting at 89.6° to 97.2° were obtained. An additional 0.1 gram of product was obtained by rinsing the reaction tube and extracting the aqueous filtrate with petroleum ether. Recrystallization by solution in aqueous alkali and acidification with hydrochloric acid raised the melting point to 98–100° and this recrystallized product did not depress the melting point of an authentic sample of 4-*tert*-butylphenol.

EXTENSION TO PENTENES

The reaction may be extended to the pentenes, 2-methyl-1-butene and 2-methyl-2-butene.

Thus, 1.56 grams of 2-methyl-1-butene were distilled into an absorption tube containing 2.0 grams of phenol and 0.2 gram of 75% sulfuric acid. The mixture was heated for 1 hour at 125° C. and poured into 20 ml. of water. There were thus obtained 2.60 grams of nearly colorless needles of 4-*tert*-pentylphenol, melting point 82° to 90° C., which after two crystallizations from petroleum ether melted at 94° to 96° C. and did not depress the melting point of an authentic sample of 4-*tert*-pentylphenol. Correspondingly, 1.7 grams of 2-methyl-2-butene reacted with 2.3 grams of phenol containing 0.2 gram of 75% sulfuric acid and gave 2.74 grams of crude 4-*tert*-pentylphenol, melting at 83° to 91°. After two crystallizations from petroleum ether, the purified product melted at 94° to 96° C.

Although these two pentenes give the same *tert*-pentylphenol, they may be readily differentiated from one another by their physical constants. Thus, 2-methyl-1-butene boils at 31.0° C. and has n_D^{20} 1.3777 (*5*), whereas 2-methyl-2-butene boils at 38.4° C. and has n_D^{20} 1.3878 (*5*).

ACKNOWLEDGMENT

The authors are indebted to Clora B. Heath for checking the method and for testing its applicability to the synthetic mixtures.

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Received September 10, 1948.

Chemical Estimation of Tetraethyl Pyrophosphate

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The biologically active tetraethyl pyrophosphate content of the technical grade product and of the so-called "hexaethyl tetraphosphate" can be determined by a method which involves the preferential hydrolysis of the accompanying polyphosphoric acid esters in a 25% aqueous acetone solution at room temperature and the absorption of these products on an Amberlite IR-4B resin, followed by the alkaline hydrolysis of the column effluent containing the tetraethyl pyrophosphate by excess standard base and back-titration with standard acid.

THE chemical estimation of tetraethyl pyrophosphate presented here was developed during an investigation of so-called "hexaethyl tetraphosphate" made by either the Schrader (*4*) or Woodstock (*6*) process. Hall and Jacobsen (*3*) have reviewed the properties and preparation of hexaethyl tetraphosphate and of tetraethyl pyrophosphate and have concluded that the latter is the biologically active constituent. Toy has recently presented a new method for the preparation of several tetraalkyl pyrophosphates including tetraethyl pyrophosphate (*5*).

The only method published to date (*2*) for the chemical estimation of tetraethyl pyrophosphate involves initial extraction of the active ingredient from an aqueous solution by chloroform. The tetraethyl pyrophosphate in the extract is subsequently hydrolyzed by heating to 50° C. overnight to form diethyl orthophosphate, which is then determined by titration with standard alkali.

[After this manuscript was submitted for publication a paper on determination of tetraethyl pyrophosphate in mixtures of ethyl phosphate esters was published (*1*). Tetraethyl pyrophosphate is removed from mixtures of ethyl phosphate esters by a benzene extraction after selective hydrolysis of the higher polyphosphate esters. It is subsequently determined by hydrolysis with alkali.]

In the new and improved procedure for estimation of tetraethyl pyrophosphate in the technical grade product or in the hexaethyl tetraphosphate the sample is first dissolved in 25% aqueous acetone. The ethyl polyphosphates are hydrolyzed rapidly to acidic products which are removed by an acid-absorbing resin, Amberlite IR-4B. Under the same conditions tetraethyl pyrophosphate is not appreciably hydrolyzed and remains in solution. Alkaline hydrolysis of the latter to the diethyl orthophosphate is effected subsequently by an excess of standard base and this excess is determined by titration with standard acid.

MATERIALS AND APPARATUS

Acetone, 25% solution in water. Five hundred milliliters of acetone, commercial grade, are mixed with 1500 ml. of water and cooled to 25° C.

Sodium hydroxide, 0.1 *N*.

Hydrochloric acid, 0.1 *N*.

Amberlite IR-4B resin, analytical grade, Resinous Products and Chemical Company, Philadelphia, Pa., obtained from Fisher Scientific Co., St. Louis, Mo.

Beckman pH meter, Model G, or any other good glass electrode apparatus.

Methyl red indicator, 0.1% aqueous solution.

Preparation and Use of Resin Column. Thirty grams of Amberlite resin, screened to remove all particles under 30-mesh, are slurried with water and poured into a 100-ml. buret contain-

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