

above ratio increases the total yield and greatly facilitates stirring.

From the results of the foregoing conclusions two large-scale runs were made in each of which 3 moles of crude *n*-butyl chlorosulfonate prepared according to Barkenbus and Owen⁵ and used without distillation was added slowly to 27 moles (2106 g.) of benzene (dried over sodium) and 6 moles (800 g.) of anhydrous aluminum chloride (technical) with stirring at 0–5°. After the elapse of three hours the mixture was poured onto 5 kg. of cracked ice, washed with concentrated hydrochloric acid and water and allowed to stand overnight with concentrated ammonium hydroxide, which readily removed labile chlorine compounds. The benzene was then washed repeatedly with 80% sulfuric acid until the acid no longer developed a color. This treatment removed unsaturated material, which has a tendency to decompose in distillation. No sulfonates could be isolated from this fraction. After washing with sodium hydroxide, drying over calcium chloride, and distillation of the excess benzene, a total residue of 652 g. remained.

Preliminary fractionation in a short column removed about 60 g. of chlorobenzene which boiled at 128–130° and was identified as *p*-nitrochlorobenzene by nitration. Much chlorine still remained and was removed by heating with sodium. Fractionation of the mixture on a large column similar to that described by Tongberg, Quiggle, and Fenske⁶ was performed at 3 mm. and many small fractions were collected. By taking the index of refraction of each fraction and plotting against the amount distilled two main fractions of constant index were obtained. The first main fraction weighing 83 g. was identified as *s*-butylbenzene by the method of Reilly and Hickenbottom:⁷ m. p. of acetamino derivative 124–125°; listed m. p. 125–126°; n_D^{20} 1.4910. Ipatieff⁸ gives 1.4902. The second fraction weighing 165 g. was characterized as *m*-di-*s*-butylbenzene by oxidation to isophthalic acid and

conversion of the latter to its methyl ester (m. p. 67–68°); n_D^{20} 1.4890; b. p. 88–92° at 3 mm. This fraction contained a trace of the ortho isomer as shown by the fluoresecein test: yields, *s*-butylbenzene, 19%; *m*-di-*s*-butylbenzene 26.6%; chlorobenzene 11.2%.

Toluene.—Six moles of *n*-butyl chlorosulfonate was allowed to react with 12 moles of aluminum chloride and 54 moles (4968 g.) of toluene for three hours after addition of the ester at –2°. The product was washed and fractionated in a manner analogous to that used for benzene. The following products were separated and identified: *m*-*s*-butyltoluene 290 g. (32.4%); b. p. 193–197°; n_D^{20} 1.4957. This fraction was completely soluble in concd. sulfuric acid; *p*-*s*-butyltoluene 174 g. (19.6%); b. p. 201–202°; n_D^{20} 1.4950. Only a trace of this fraction was soluble in cold concd. sulfuric acid; *o*-chlorotoluene 83 g. (21.8%). The *o*-chlorotoluene and *p*-chlorotoluene fractions were not pure but were contaminated slightly with each other, due to the closeness of their boiling points. They were of sufficient purity to obtain readily *o*-chlorobenzoic and *p*-chlorobenzoic acid by oxidation of the respective fractions: *p*-chlorotoluene 23.5 g. (6.2%). A high boiling hydrocarbon residue of 170 g. also was obtained but the components were not identified. Considerable benzoic acid, probably derived from benzotrichloride, resulted from the sodium treatment and smaller amounts of other side-chain chlorinated products were present.

Summary

The action of *n*-butyl chlorosulfonate on benzene and toluene in the presence of anhydrous aluminum chloride has been investigated. The principal effect is one of alkylation accompanied by nuclear and side-chain chlorination.

n-Butyl chlorosulfite reacts with benzene and aluminum chloride to produce *s*-butylbenzene. The reaction is not accompanied by chlorination, but sulfur derivatives are produced.

LEXINGTON, KENTUCKY

RECEIVED MAY 27, 1939

(5) Barkenbus and Owen, THIS JOURNAL, **56**, 1206 (1934).

(6) Tongberg, Quiggle and Fenske, *Ind. Eng. Chem.*, [11] **26**, 1212 (1934).

(7) Reilly and Hickenbottom, *J. Chem. Soc.*, **117**, 120 (1920).

(8) Ipatieff, Corson and Pines, THIS JOURNAL, **58**, 919 (1936).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Fractionation of the Hydrogen Isotopes in the Distillation of Ethyl Alcohol

BY ALEX H. WIDIGER AND WELDON G. BROWN

During the course of some experiments on hydrogen exchange reactions in deuterio-alcohol in which it was necessary to recover the alcohol from the mixtures, for deuterium analysis, by careful fractional distillation under reduced pressure, using small laboratory columns, we had occasion to suspect that serious errors were being introduced as a result of fractionation of the hydrogen isotopes during the distillations. In view of the small mass difference between C_2H_5OD and

C_2H_5OH , and the difficulty of accomplishing the desired separations (*e. g.*, phenylacetylene and alcohol) with our columns, the possibility of accounting for our results on this basis was not considered seriously until after a number of more obvious possible sources of error had been eliminated. It was nevertheless possible to show, by distillations of alcohol alone, that the degree of isotopic separation is fully capable of accounting for our results.

The first distillations were carried out with a vacuum-jacketed column, 4 mm. i. d., 45 cm. in length, containing a spiral nichrome wire packing. In a typical experiment, a sample of alcohol containing 17.8% C_2H_5OD was distilled at 40 mm. pressure, and the distillate, amounting to one-half of the total, was found to contain 14.8% C_2H_5OD . The boiler residue was correspondingly richer in deuterium and contained 21.1% C_2H_5OD . In order to compare this separation with that to be obtained on the distillation of water, a sample of water containing 3.06% D_2O was distilled under similar conditions and the distillate was found to contain 2.43% D_2O . These results would indicate that the fractionation of the hydroxyl hydrogen in alcohol takes place with very nearly the same efficiency as the fractionation of the isotopic forms of water. However, some allowance would have to be made for the fact that this column could not be made to operate smoothly in distillations of water.

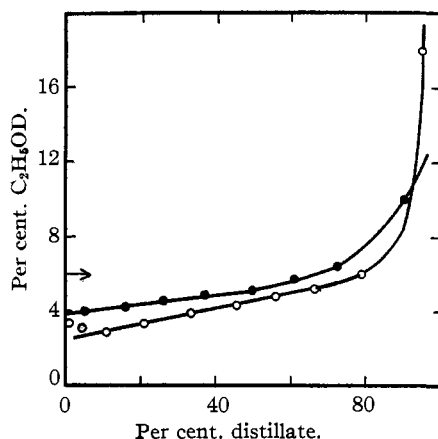


Fig. 1.—The distillation of 6% C_2H_5OD at atmospheric pressure (●) and at 80 mm. (○).

These results immediately suggested that the distillation of alcohol with the aid of high efficiency fractionating columns might prove to be a practicable method for the concentration of deuterium in quantity. The concentration of deuterium by the distillation of water has not thus far been a conspicuous success and it appears to be common experience that the efficiency of fractionating columns in such distillations does not approach that predicted on the basis of performance with organic liquids. The method of distilling alcohol offers a number of advantages from the standpoint of column operation and it was therefore of interest, although there is no intention of pursuing the project further at this time, to determine the degree of isotope separation obtainable with a more efficient column than that described above.

Subsequent distillations were carried out using a column packed with single-turn glass helices, packed length 2.2 m., internal diameter 18 mm. The theoretical plate equivalent of this column was estimated to be in the neighborhood of 25 plates, this estimate being based on its performance in the separation of active amyl and isoamyl alcohols.¹ The results of two distillations, one at atmospheric pressure (750 mm.), the other at 80 mm. pressure, of deuterio-alcohol containing 6.0% C_2H_5OD initially are shown in Fig. 1. The isotopic separation obtained corresponds to a fractionation factor 1.6 for the distillation at atmospheric pressure, and a factor 2.4 for the distillation at 80 mm. pressure. Assuming a column efficiency of 25 plates, the enrichment factors for the vaporization process are as follows: at 750 mm. 1.019 and at 80 mm. pressure 1.035.

In a distillation at atmospheric pressure of water containing 0.330% D_2O , the first fraction of the distillate was found to contain 0.195% D_2O . Before this experiment was carried out the column was cleaned thoroughly by distilling nitric acid through it, in order to facilitate uniform wetting of the packing, and no difficulty was experienced in the subsequent operation of the column with pure water. The observed fractionation factor, 1.69, is slightly higher than that found in the distillation of alcohol, and if we again assume a column efficiency of 25 plates we obtain an enrichment factor, 1.021. This is appreciably lower than the value, 1.025, reported by Urey and Teal² and our estimate of the column efficiency was therefore, for this distillation at least, too high.

The fact that a partial separation of the hydrogen isotopes can be effected readily by the distillation of water has been known for some time³ and consequently the possibility of errors arising from this source in work on exchange reactions in heavy water has been recognized almost from the beginning. It is now evident that effects of this type can be equally significant in work on exchange reactions in heavy alcohol and that the necessary precautions will have to be taken to minimize the resulting errors.

Summary

It has been shown, by distillations of alcohol in laboratory fractionating columns, that the isotopic forms, C_2H_5OH and C_2H_5OD , readily undergo a partial separation on distillation, the degree of isotopic separation being comparable with that observed in the distillation of water.

CHICAGO, ILLINOIS

RECEIVED JULY 7, 1939

(1) The work on the amyl alcohols was carried out by Mr. W. deAtley.

(2) H. C. Urey and G. K. Teal, *Rev. Modern Phys.*, **7**, 48 (1935).

(3) E. W. Washburn and E. R. Smith, *J. Chem. Phys.*, **1**, 426 (1933); G. N. Lewis and R. E. Cornish, *THIS JOURNAL*, **55**, 2616 (1933); N. F. Hall and T. O. Jones, *ibid.*, **56**, 749 (1934).