6. The phenyl linkage is broken down when triphenylsilicyl chloride is reduced with metallic sodium in liquid ammonia. Triphenylsilicyl chloride hydrolyzes in liquid ammonia with the formation of triphenylsilicylamine and ammonium chloride.

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THE CATALYTIC PREPARATION OF ETHER FROM ALCOHOL BY MEANS OF ALUMINUM OXIDE

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Introduction

Considerable work has been done on the dehydration of alcohol in the gaseous phase by means of solid catalysts, and of all catalysts alumina now appears to be the most efficient. The optimum temperature recommended by Senderens[1] for the production of ether by this means is 250°; above this temperature increasing amounts of ethylene are formed. Pure ether is also dehydrated to ethylene at temperatures above 250°. Senderens reports his best yield of ether from a catalyst prepared by precipitating aluminum hydroxide from sodium aluminate with sulfuric acid. He considers this form of alumina better than that obtained by precipitating the hydroxide from aluminum salts by ammonia. Senderens does not give any detailed information about the preparation of the catalyst, nor about the yields obtained.

Mailhe and de Godon[2] report a 71% yield of ether at 190°, using anhydrous aluminum sulfate as catalyst.

Pease and Yung[3] obtained a 60% yield of ether at 250° with alumina prepared from aluminum nitrate and ammonia. Ipatiew[4] obtained an appreciable amount of alcohol from equimolecular quantities of ether and water, thereby showing the reaction to be reversible.

It is generally considered that the nature of the surface of the catalyst plays a considerable part in the activation of the reaction. The idea that the spacing of atoms or molecules is a factor in catalytic reactions at surfaces has been considered by Langmuir.[5] Further experimental evidence of this has been given by Adkins,[6] for reactions similar to that

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[1] Senderens, *Ann. chim. phys.*, [8] **25**, 505 (1912).

[2] Mailhe and de Godon, *Bull. soc. chim.*, **25**, 565 (1916).

[3] Pease and Yung, This Journal, **46**, 390 (1924).

[4] Ipatiew, *Ber.*, **37**, 2986 (1904).

[5] Langmuir, *Trans. Faraday Soc.*, **17**, 617 (1922).

[6] Adkins, This Journal, **44**, 385, 2175 (1922); **45**, 809 (1923); **46**, 130 (1924).

under consideration here. Consequently an endeavor has been made in this investigation to prepare catalysts in various ways, in order to determine the catalyst most efficient in the production of ether.

During the course of this investigation two papers on this reaction have appeared by Pease and Yung.[4,7] In the latter paper, the authors find an equilibrium corresponding to a maximum conversion of alcohol to ether of 62% at 275°. Calculations from their data would show the equilibrium to correspond to a maximum conversion of 66% at 250°. Our results, on the other hand, show yields of over 80% at this temperature. Pease and Yung, moreover, state that their product did not separate into two layers. The fact, alone, that our product and also that of Senderens separated into two layers would indicate yields considerably higher than 66%.

Apparatus and Procedure

The arrangement of the apparatus is shown in Fig. 1. The procedure consisted in passing a definite volume of liquid alcohol into a hot tube filled with the catalyst. The alcohol vaporized on contact with the hot surface of the tube. The vapors then passed on over the catalyst and out through a condenser, the liquid products being retained in a bulb attached to the condenser and the gases passed over to an aspirator containing a saturated salt solution. Before a run was made, for analysis about 15 cc. of alcohol was passed over the catalyst to make sure that the catalyst was functioning uniformly.

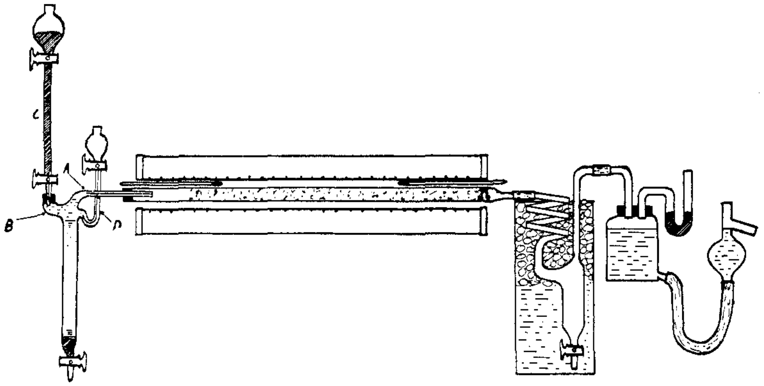

Fig. 1.—Apparatus.

The alcohol was introduced from a graduated vessel by a modification of Adkins and Nissen's[8] method.

A capillary tube A bent at right angles was sealed onto the top of a buret; a side tube B bent upward at right angles was sealed into the buret near the top; a dropping

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[7] Pease and Yung, This Journal, **46**, 2397 (1924)

[8] Adkins and Nissen, *ibid.*, **46**, 130 (1924).

funnel C, with a capillary tube stopcock sealed to the end of its stem, was inserted into the side tube of the buret through a cork; a second dropping funnel D was sealed into the buret near the top for refilling the apparatus with alcohol. Capillary tube A led into the catalyst tube. Mercury was allowed to drop at a controlled rate from the dropping funnel C into the buret, forcing the alcohol into the catalyst chamber. The volume of the alcohol passed over the catalyst was read from the buret. The apparatus could be left connected to the furnace for several runs, the method was easily controlled and quite satisfactory for a liquid as volatile as alcohol. The temperature was measured by means of long thermometers inserted in both ends of the furnace. The furnace was electrically heated, and no difficulty was experienced in regulating the temperature. The catalyst was ground and almost filled a Pyrex tube 120 cm. in length and 1.6 cm. in diameter.

An efficient condenser and receiving bulb were made in one piece and as light as possible for weighing. A spiral of glass tubing was sealed into a bulb, to which was also sealed a straight vertical tube to allow the escape of ethylene to the aspirator. The condensed liquid was removed through a stopcock at the bottom of the bulb. The condenser was kept in an ice-bath; the amount of ether carried over with the ethylene was found to be negligible. The pressure in the reaction chamber was atmospheric.

The Method of Analysis

The method of analysis selected was that employed by Pease and Yung,[7] and the ether salted out by saturated sodium chloride solutions. These authors give a correction chart on which the observed volumes of ether separating are plotted against the true volume. Their curve shows that when the yield of ether is low the separation is greater than the true volume, and that when the yield is high the separation is less.

In attempting to duplicate their results, values were obtained which coincided with those given for the higher yields but not for the lower, the volume separating in all of our experiments being less than the true volume. Preliminary experiments showed that it would be necessary to make up known mixtures, in which the products would be in the same proportion as would be formed in the reaction mixtures, according to the equation, $C_2H_5OH = (C_2H_5)_2O + H_2O$.

Amounts of ether, alcohol and water in the required proportions, measured at room temperature (15°) were run from burets into a 100cc. flask, to the neck of which was sealed a 50cc. buret. After the addition of 100 cc. of saturated salt solution, the flask was corked and suspended in a bath at 10°, and was repeatedly shaken until complete equilibrium between the two layers was attained. When the temperature of the mixture became constant at 10° the volume of the separating layer was read.

Absolute alcohol and ether were used in all the measurements. The density of the alcohol was 0.793 at 15°; that of the ether, 0.719 at the same temperature.

Table I gives the results obtained when the ether, alcohol and water were in a proportion corresponding to the percentage conversion given in Col. 1, the total products in all cases being equivalent to 20 cc. of alcohol.

TABLE I

VOLUME OF ETHER FOUND VERSUS TRUE VOLUME

Conversion, %	Ether, cc.	Alcohol, cc.	Water, cc.	Vol. separating Cc.	Correction Cc.
100	17.8	0.0	3.1	16.4	1.4
90	16.0	2.0	2.8	14.7	1.3
80	14.3	4.0	2.5	13.1	1.2
70	12.4	6.0	2.2	11.25	1.15
60	10.7	8.0	1.9	9.6	1.1
50	8.9	10.0	1.6	7.9	1.0
40	7.1	12.0	1.2	6.2	0.9
30	5.3	14.0	0.9	4.4	.9
20	2.5	16.0	.6	1.4	2.1

The results recorded in Table I and plotted in a correction chart (Fig. 2) were duplicated with a variation of less than 1%, which would be the limit of error in the determination of ether resulting from the dehydration of alcohol, where the yield is 30% or over. This chart was employed in all subsequent analyses.

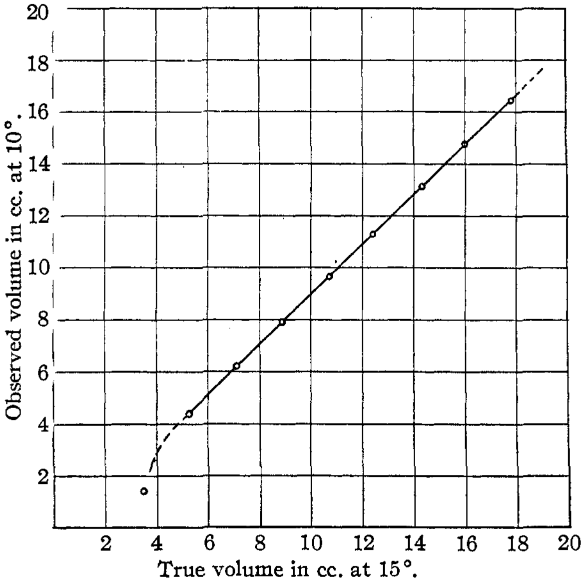

Fig. 2.—Correction chart for ether determination.

Preparation of Catalysts

Among the best catalysts tried were the following.

Catalyst A.—An 8% solution of sodium aluminate, which by analysis was found to have the ratio Al_2O_3:Na_2O::1:2, was precipitated by slowly adding an equivalent quantity of 0.25 *N* sulfuric acid. The precipitate was washed with cold water by decantation until it no longer contained sulfate, after which it was washed again with hot water and dried by gradually heating to 400°; best yield, 74.3%.

Catalyst B.—A 10% solution of the same sodium aluminate was slowly precipitated by carbon dioxide. The precipitate was washed and heated to 350° in the same manner; maximum yield, 79.4%.

Catalyst C.—A 10% solution of the same sodium aluminate, on standing, soon began to hydrolyze, precipitating aluminum hydroxide. The precipitate was washed as before, but after drying contained traces of alkali. The precipitate was then heated to 400° and again washed several times in nearly boiling water. This process of heating and washing was repeated until finally the product was neutral to phenolphthalein.

Catalysts of both Types B and C which still retained alkali were found to give very poor yields, under 50%. Such catalysts, however, when repeatedly heated and washed finally gave yields of 70–80%. Catalysts of these types were found to be just as reactive after 1500 cc. of alcohol was passed over them as at first.

The catalysts obtained by Method C were the most difficultly soluble in acids of any tried and gave the highest yields, 80%.

Experimental Data

All of these experiments were carried out at 250°. The best rate of flow of the alcohol varied with the different catalysts, ranging from 15 to 20 cc. per hour. At more rapid rates of flow the total dehydration fell off and at slower rates the yields of ethylene increased at the expense of the ether—a result also found by Pease and Yung.

A check was made on all possible loss of alcohol or the products of the reaction by weighing the condenser and contents and calculating the weight of ethylene from its volume. The sum of these weights checked with the weight of the alcohol used in all cases. The analyses are considered to be accurate within 1%.

Some of the results are tabulated in Table II. The column headed drying temperature refers to the temperature to which the catalyst was heated in drying before use. The reactants and products were measured by volume throughout and their weights calculated.

Table II

Formation of Ether from Alcohol

Catalyst	Time of run. Min.	Drying temp. ° C.	Alcohol, g.	Ether, g.	Ethylene, Cc.	% Conversion to ether	% Conversion to ethylene
A	95	400	16.80	9.50	750	70.5	9.2
A	63	400	17.15	9.80	590	71.0	7.1
A	57	400	16.65	9.83	480	74.3	5.9
B	110	350	16.62	10.65	210	79.4	2.6
B	95	400	16.50	10.20	380	78.0	4.7
B	96	400	16.56	10.56	300	79.1	3.7
C	69	400	16.60	10.80	180	80.8	2.2
C	107	400	16.60	10.80	220	80.8	2.7
C′	67	420	16.55	10.43	300	78.5	3.7
C′	63	420	16.50	10.73	340	80.5	4.2

Effect of Re-running the Products.—One hundred cc. of alcohol was passed over Catalyst C, and proportionate amounts of the two layers, giving a total volume of 20 cc., were analyzed. The remaining product was then passed over the catalyst again, the two layers being introduced in rates proportional to their amounts by means of two droppers united by a common delivery tube. This process was repeated to see whether the yield of ether could be further increased; the amount of ether was found, however, to be slightly lower than before. This decrease was due to an increase of ethylene at the expense of the ether.

Formation of Alcohol from Ether and Water.—The reversibility of the reaction has been shown by Ipatiew and later by Pease and Yung. Table III gives the results of two experiments in which ether and water in equimolecular proportions were passed over Catalyst C by means of the double dropper. The products on analysis showed that the ether had decreased by an amount considerably greater than the equivalent of ethylene formed. The column headed alcohol is the amount of alcohol theoretically equivalent to the ether and the water used.

TABLE III

FORMATION OF ALCOHOL FROM ETHER AND WATER

Time of run, min.	Wt. used, g. Ether	Water	Alcohol equivalent	Ether recovered, G.	Ethylene Cc.	Alcohol formed G.	%	Ethylene, %
62	13.40	3.30	16.65	11.37	200	2.03	12.2	2.4
56	13.60	3.40	16.90	11.95	150	1.84	11.0	1.8

As is seen from Table III, about 12% of the alcohol equivalent of the mixture is obtained as alcohol. The formation of ethylene makes it difficult to arrive at an exact equilibrium value for the reaction $2C_2H_5OH = (C_2H_5)_2O + H_2O$. From the measurements recorded in Tables II and III, the equilibrium may be estimated to correspond to a yield of 85% of ether, or the equilibrium constant would have a value of 8. From this value of the equilibrium constant and the thermal data collected by Pease and Yung,[7] the maximum possible conversion of alcohol to ether at 275° would be 82.5%, which is much higher than found by them experimentally.

Summary

1. A study has been made of the catalytic dehydration of ethyl alcohol to ether in the gaseous phase in the presence of alumina at 250°.
2. The maximum percentage of ether was obtained from the catalyst prepared by dehydration of the crystalline aluminum hydroxide resulting from the spontaneous decomposition of solutions of sodium aluminate. The highest yield was obtained at 250° and amounted to 80.8%.
3. Alcohol was obtained from equimolecular quantities of ether and water, showing the reaction to be reversible. The position of equilibrium has been determined at 250° to correspond to a maximum possible con-

version to ether of about 85%. The corresponding equilibrium constant is 8.0.

4. It has been found that absolute purity of the catalyst is essential. Impurities may be more quickly and completely removed by alternately heating to 350° and washing again.

5. Heating the catalyst to about 400° but not higher, in drying, was found to give the most active product.

6. The catalysts prepared as described retain their activity, unimpaired, after long use.

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THE NITRATION OF HEXAMETHYLENETETRAMINE[1,2]

BY GEORGE C. HALE

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Introduction

Hexamethylenetetramine possessing weakly basic properties reacts with acids to form salts. Thus the phenate,[3] citrate,[4] camphorate[5] and perchlorate[6] of the base have been prepared and patented for use as pharmaceutical compounds. Ischidzu and Inouye[7] reported that the tetramine is decomposed by hydrochloric, sulfuric, acetic, succinic and salicylic acids to give chiefly formaldehyde, ammonia, carbon dioxide and methylamine. The relative amounts of the different decomposition products formed depend on the concentration of the acid used, the temperature and the duration of the action.

With regard to the action of nitric acid on hexamethylenetetramine, Henning[8] has reported that the amine does not lend itself to the usual methods of nitration, as it is decomposed into formaldehyde and ammonia. However, he described a method for preparing a nitro compound of the formula $C_3H_6O_6N_6$, which involves treating an aqueous solution of hexamethylenetetramine with nitric acid to obtain hexamethylenetetramine nitrate and then adding the dried nitrate in small portions to nitric acid, d. 1.52, cooled to —5°; after the mixture is allowed to stand in the cold for half an hour and is then poured into ice water, the nitro compound separates in the form of colorless crystals. These crystals are said to melt

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[1] This paper is prepared from a thesis submitted by G. C. Hale to the Faculty of the Graduate School of Indiana University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Published by permission of the Chief of Ordnance.

[3] E. Defrance, *J. Pharm. Belg.*, **3**, 605 (1921).

[4] Brit. pat. 26,160, Nov. 22, 1911.

[5] U. S. pat. 1,064,227, June 10, 1913.

[6] Ger. pat. 292,284, July 27, 1915.

[7] Ischidzu and Inouye, *Chem. Centr.*, **77**, 1087 (1906).

[8] Henning, Ger. pat. 104,280, June 14, 1899.