[Contribution from the Chemical Laboratory of Loyola University]

CATALYTIC DEHYDRATION OF ETHANOL BY ALUMINA AT VARIOUS TEMPERATURES

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Pease and Yung[1] report that the maximum yield of ether at 275° is 62.00%. Clark, Graham and Winters[2] report yields of ether of over 80.00% at this temperature. It was with the view of determining which of these investigators was right and of throwing further light on the mechanism of the reactions involved in the decomposition of ethanol by alumina that this investigation was undertaken.

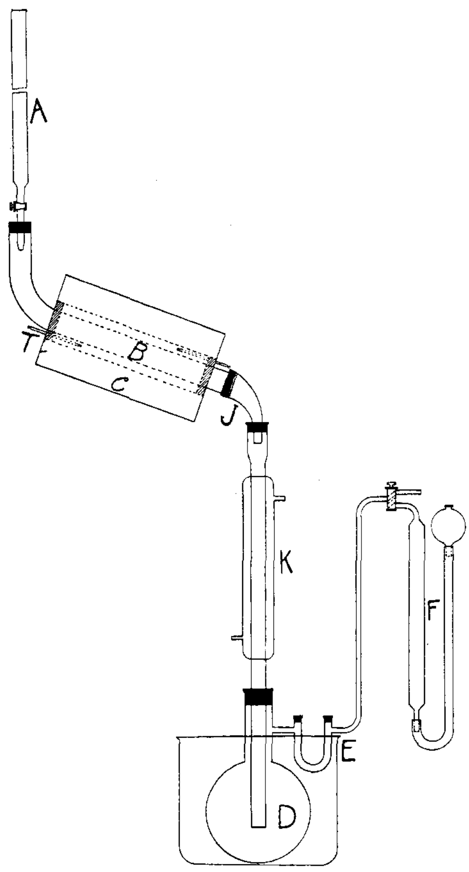

Fig. 1.

Materials

Ethyl Alcohol.—The alcohol was prepared according to the method described in a previous paper.[3]

Alumina Catalyst.—The aluminum oxide was prepared by precipitation with ammonium hydroxide from a dilute solution of the nitrate; the solution was boiled to expel the excess of ammonia, the precipitate allowed to settle and the clear supernatant liquid decanted. The precipitate was washed eight times with conductivity water and then filtered through a smooth, hardened filter. The precipitate was dried for eighteen hours at 240–250°.

Apparatus and Procedure

The apparatus is shown in Fig. 1. A definite volume of alcohol (40 cc.) was allowed to drop at a controlled rate from a buret A into the catalyst

[1] Pease and Yung, This Journal, **46**, 390, 2397 (1924).

[2] Clark, Graham and Winters, *ibid.*, **47**, 2748 (1925).

[3] Pearce and Alvarado, *J. Phys. Chem.*, **29**, 256 (1925).

Tube B filled with the catalyst, the temperature of which was held constant in an electrically heated furnace C.

The catalyst tube B consisted of a Pyrex tube 2 × 54 cm. and was bent as shown in the figure for convenience of manipulation. The furnace was mounted at an angle of 20° to insure proper drainage of the liquid products. The catalyst tube was connected to the condenser K by means of the adapter J. The liquid products were collected in the distilling flask D, completely immersed in a freezing-bath. The gaseous products passed through the side arm of the flask, first into a U tube E, also immersed in a freezing-bath, and then to the gas measuring buret F. The amount of ethylene produced in the reaction was determined by the method of Pease and Yung;[1] the amount of ether by that of Clark, Graham and Winters.[2] The table given by these investigators was used in correcting the observed volumes of ether.

Experimental and Discussion

The results obtained are given in Fig. 2; curves I, II and III represent the ether curves at 269, 300 and 354°, respectively, while IV, V and VI

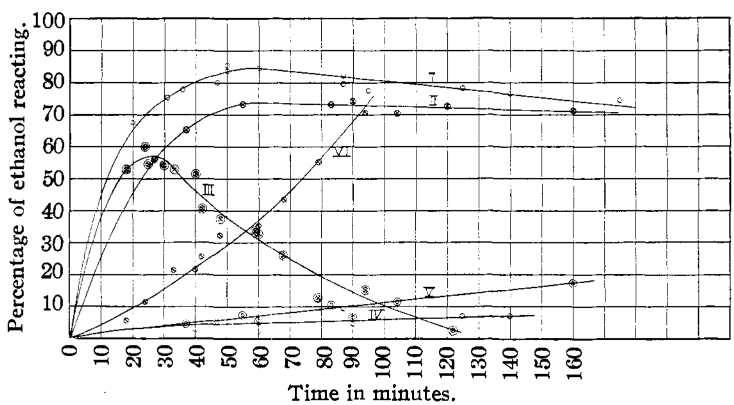

Fig. 2.

are the corresponding ethylene curves at the same temperatures. An examination of the curves shows that for corresponding times of contact the fraction of ethanol appearing as ether becomes less and less as the temperature increases or, for the same temperature, the fraction appearing as ether becomes less and less as the time of contact is lengthened, the change in the slopes of the curves being more marked at the higher than at the lower temperatures. This seems to indicate that the dehydration of ethanol by alumina is at least a two stage process, the first being the production of ether and the second the dehydration of this ether to ethylene. For a given catalyst the relative proportions of ether and ethylene appear to be dependent upon the temperature and time of contact. The results here given show that at each temperature the yield of ether passes through a maximum as the time of contact is lengthened. The yield of ethylene, on the other hand, increases continuously. This is in agreement with the results of Pease and Yung[1] at 300°. The maximum yields of ether are, however, higher than those reported by Pease and Yung[1] and are as high as the best yields reported by Clark, Graham and Winters.[2] These maximum yields amount to 82.20% at 269°, 73.50% at 300° and 55.00% at 354°. Pease and Yung[1] report 62.00% at 275°; Clark, Graham and Winters[2] report 85.00% at 275°. The author obtained 82.20% at 269°. The indication is that the higher value is more nearly correct.

Summary

1. The dehydration of ethanol by alumina has been studied at 269, 300 and 354°, respectively, and the results are plotted.
2. Maxima in the ether yields have been obtained at 269, 300 and 354°.
3. The maximum yield of ether at 269 corresponds to 82.20%.
4. A reasonable explanation has been offered for the mechanism of the reactions taking place in the dehydration of ethanol by alumina at the temperatures studied.

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[CONTRIBUTION FROM THE UNIVERSITY CHEMICAL LABORATORIES, UNIVERSITY OF THE PUNJAB]

ESTIMATION OF $-SOOH$ (SULFINIC) GROUP AND FE^{+++}

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In a paper on the "Isolation of Sulphinic Acids," Thomas[1] has shown that sulfinic acids give a voluminous precipitate when treated with solutions of ferric salts in strongly acid solutions. These orange colored ferric salts on analysis are found to be of the general formula $(RSOO)_3Fe$, and are insoluble in water and in dilute mineral acids. They are, however, decomposed by alkalies, giving ferric hydroxide and salts of the corresponding sulfinic acids. Sulfinic acids, as a class, have thus been characterized by this property of yielding ferric sulfinates.

It was therefore found desirable to investigate the formation of such ferric salts on quantitative lines, and to employ this method for the estimation of $-SOOH$ group in organic compounds. The importance of this is apparent when it is known that sulfinic acids, which are fairly strong acids, cannot be estimated by titration against standard alkalies when other negative groups (such as, COOH, SO_3H, etc.) are present in the molecule.

[1] Thomas, *J. Chem. Soc.*, **95**, 342 (1909).