

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE TRANSFER OF HYDROGEN FROM AN ALCOHOL TO AN ALDEHYDE.

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Historical.

Since it has become known that, in presence of certain catalysts, alcohols and hydro-aromatic compounds set free hydrogen, and that certain other compounds are hydrogenated under similar conditions, a number of efforts have been made to combine the two processes, utilizing the hydrogen liberated in the one to supply the hydrogen required by the other. If this can be accomplished, many difficulties which are met with in the manufacture of pure hydrogen are avoided and, if the substance which gives up its hydrogen is worth more for the loss, as is the case when ethyl alcohol passes into the more valuable acetaldehyde, the cost of the hydrogen is eliminated.

The ideal case is one in which the dehydrogenation of the one substance and the hydrogenation of the other take place with the same catalyst and at the same temperature.

For the reaction to go, the energy change must be in the right direction, as a catalyst cannot be expected to push anything up hill.

Both of these conditions are fulfilled in the case studied by Zelinski and Glinka¹ who treated methyl tetrahydro-terephthalate with palladium and obtained the terephthalate and the hexahydro-terephthalate, one portion of the tetrahydro- giving off hydrogen which was taken up by the other. In this case the energy change is in the right direction since the partially hydrogenated benzene ring is less stable than the fully hydrogenated or the unhydrogenated.

Bösesken² has studied a similar case. He passed dihydro-benzene, and also tetrahydro-benzene, over nickel at 180°, and he sealed up the latter hydrocarbon with palladium for some time. In all cases a mixture of benzene and cyclohexane was obtained. He gives as the heat of combustion of dihydro-benzene 847.5 Cal. and that of a mixture of 1/3 benzene and 2/3 cyclohexane 832.5 Cal., the difference being 15.0 Cal. The reaction went as was expected.

Meyer and Eckert³ mention the dehydrogenation of ethyl alcohol to acetaldehyde and the addition of the hydrogen to benzoquinone or thymoquinone with the formation of the corresponding quinols, under the influence of light.

Armstrong and Hilditch⁴ transformed a mixture of cyclohexanol by the action of nickel into cyclohexanone and methyl phenylpropionate.

Padóa and Foresti⁵ made a quantitative study of the transfer of hydrogen from *iso*-propyl alcohol to diethyl ketone and to benzene, with the formation of diethyl

¹ Zelinski and Glinka, *Ber.*, **44**, 2305 (1911).

² Bösesken, *Rec. trav. chim.*, **37**, 255 (1918).

³ Meyer and Eckert, *Monatsh.*, **39**, 241 (1918).

⁴ Armstrong and Hilditch, *Proc. Roy. Soc.*, **96A**, 322 (1917).

⁵ Padóa and Foresti, *Atti. accad. Lincii*, **23**, II, 84 (1914).

carbinol and cyclohexane, respectively. They found equilibria corresponding to those calculated from the Nernst heat theorem.

Sabatier and Murat⁶ passed the vapors of alcohols with benzaldehyde, benzophenone, benzyl alcohol and acetophenone over thoria at 420° and got complete reduction to toluene, ethylbenzene and diphenyl methane.

Kayser⁷ has patented the hydrogenation of unsaturated oils by heating them with borneol or *iso*-borneol in the presence of nickel.

The Present Investigation.

In our study we have used ethyl alcohol with heptaldehyde, benzaldehyde, phenyl-acetaldehyde and citronellal over ceria at 300–380° and have obtained the corresponding alcohols along with acetaldehyde. The transformation is never complete. There is considerable condensation of the aldehydes to gummy products which foul the catalyst in a short time and stop the transformation. The catalyst may be regenerated by treatment with steam followed by oxides of nitrogen and a second treatment with steam. A small proportion of manganese in the ceria appears to increase its activity. On account of the destruction of a part of the aldehyde, the amount of alcohol that can be recovered from the product is much less than the amount of aldehyde that has disappeared. A small amount of benzyl benzoate was found in the product when benzaldehyde was used.

With copper on an inert support we have obtained results similar to those of Sabatier and Murat with thoria, but at a lower temperature, 330–360°; that is, benzaldehyde is reduced all the way to toluene.

Ethyl alcohol was chosen rather than methyl on account of the greater difference between its heat of combustion and that of its aldehyde which gives a greater driving force to the reaction.

Experimental.

Ceria Catalyst.—To a solution of 30 g. of cerium nitrate in 80 cc. of water, 10 g. of fluffy asbestos was added, care being taken to prevent packing. The beaker containing this mixture was placed in an evacuated desiccator over sulfuric acid till the water had evaporated, leaving a porous mass which was cut into pieces and packed in the catalyst tube where it was heated slowly up to 180° in a current of air. Alcohol vapors were passed through the tube till the nitrate was decomposed and then steam to remove all volatile matter.

A catalyst prepared in this manner showed considerably greater activity in esterification than one prepared in the usual way by decomposing the nitrate by heat alone at 270° to 350°. With an equimolar mixture of acetic acid and ethyl alcohol with 110 cc. of vapor per minute at 250°,

⁶ Sabatier and Murat, *Compt. rend.*, 157, 1499 (1913); *Bull. soc. chim.*, [4] 15, 227 (1914).

⁷ Kayser, U. S. pat. 1,134,746; *C. A.*, 9, 1401 (1916).

64% and 42%, respectively, of esterification were obtained with the two preparations of ceria.

Apparatus and Methods.—We have used 12 g. of ceria suspended on 9 g. of asbestos in a Pyrex glass tube, the free space in the tube being estimated at 93 cc. This tube was heated in an electric tube furnace automatically regulated to $\pm 1^\circ$.

The aldehyde was mixed with 2 to 3 equivalents of ethyl alcohol, allowed to drop at the desired rate into a heated space and the vapors were passed into the catalyst tube. The volume of vapors passing through the tube was calculated from the number of drops per minute, from the weight of a known number of drops from the same tip, and from the temperature, etc.

The condensate from the furnace was distilled till the boiling point was reached, 100° to 120° , and the aldehyde determined in the residue. A blank on known mixtures gave results about 10% low when treated in the same way, hence 10% was added to the amount of aldehyde found.

The aldehyde in the product was estimated by a modification of the method of Seyewetz and Bardin⁸ as described by Kingscott and Knight.⁹ About 0.5 g. of the sample was treated with 10 cc. of a 20% solution of sodium sulfite made neutral to phenolphthalein, and the alkali set free was titrated slowly with 0.2*N* acetic acid. Vigorous shaking was necessary to complete the reaction in reasonable time, about 25 minutes being required for a titration. The addition of alcohol hastens the reaction but obscures the end-point. This method gives constant results with simple aldehydes, though somewhat low. We obtained the following results on known samples: with pure heptaldehyde, 98.8, 99.0 and 98.1%; with benzaldehyde, 97.5%; with cinnamic aldehyde, 94.0 and 93.7%; with commercial citronellal, 90.5 and 90.5%; with citral, 90.2, 91.0 and 90.5%. Since citral combines with two molecules of bisulfite the titrations with it have to be divided by 2.

Results.—Phenylacetaldehyde at 330° passed at the rate of 220 cc. of vapor per minute gave 20% of phenylethyl alcohol. Benzaldehyde gave rather less than 20%.

Cinnamic aldehyde and citral gave none of the corresponding alcohols.

The largest amount of study was put on heptaldehyde. The aldehyde was prepared by destructive distillation of castor oil and carefully purified by fractionation in a vacuum. The amount of aldehyde disappearing when heptaldehyde with 3 moles of ethyl alcohol is passed over ceria at various temperatures is given in tabular form.

⁸ Seyewetz and Bardin, *Bull. soc. chim.*, [3] 33, 1000 (1905).

⁹ Kingscott and Knight, "Methods of Organic Analysis," Longmans, Green, and Co., 1914, p. 245.

Rate per min. Cc.	Aldehyde disappearing at		
	330° %	350° %	370° %
96	76	100	95
144	76	79	83
238	70	71	77
357	61	63	78
475	45	58	72
640	73

From 60 g. of the product, collected from several runs, 15 g. of hexyl alcohol was isolated.

With citronellal, the temperature must be kept close to 315° as at higher temperatures the formation of condensation products is excessive and at lower the reaction is too slow. A mixture of 12 g. of citronellal and 10 g. of ethyl alcohol was passed over the ceria at 315° at the rate of 250 cc. of vapors per minute. The product was fractionated and the portion boiling from 180° to 230° was heated with 8 g. of phthalic anhydride for 3 hours at 100°. The monophthalic ester was dissolved in 50 cc. of 10% sodium carbonate solution and extracted several times with ether to remove non-alcohols. The ester was saponified by sodium hydroxide and the citronellal distilled with steam, yielding 6 g. or about 50%. At 300° and at 320° much smaller yields were obtained.

Sealed Tube Experiments.—A mixture of 30 g. of citronellal and 15 g. of absolute ethyl alcohol was heated in a sealed glass tube with 3 g. of the ceria-asbestos catalyst for 12 hours at 220°. After fractionation the high-boiling portion was put through the phthalic anhydride treatment and yielded 9 g. of alcohol, apparently citronellol. This was repeated, heating to 195° for 14 hours, and 12 g. of the alcohol obtained.

Summary.

By passing the vapors of aldehydes mixed with ethyl alcohol over ceria at 300–380° the aldehyde is hydrogenated to the corresponding alcohol and the ethyl alcohol is dehydrogenated to acetaldehyde. Benzyl, phenyl, ethyl and heptyl alcohols and citronellol have been thus prepared. The yields are low and the life of the catalyst is short on account of fouling, probably due to condensations of the aldehydes.

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