CATALYSIS BY ALUMINA AND ZINC OXIDE OF THE DISPROPORTIONATION OF CERTAIN ALCOHOLS, ETHERS AND HYDROXY ESTERS

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It has been shown in previous papers[1] that over alumina allyl alcohol apparently undergoes intramolecular rearrangement to form propionaldehyde according to equation (I).

$$CH_2{=}CHCH_2OH = CH_3CH_2CHO \tag{I}$$

It has also been demonstrated that alumina and zinc oxide may catalyze the reduction by alcohols of 2,3-unsaturated aldehydes such as acrolein and cinnamic aldehyde to the corresponding saturated aldehydes as indicated in equation (II).

$$CH_2{=}CHCHO + RCH_2OH = CH_3CH_2CHO + RCHO \tag{II}$$
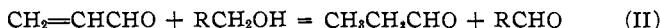
In connection with a study of the mechanism of the reactions of various organic compounds over oxide catalysts, it was considered of some importance to ascertain whether these reactions were encountered with compounds whose region of unsaturation was further removed from the alcohol or aldehyde group. In order to test this point the behavior of Δ^3,2,2-dimethylbutenol-1, $CH_2{=}CHC(CH_3)_2CH_2OH$, over alumina and zinc oxide was studied. The structure of this compound is such that the double linkage cannot migrate to the 2,3-position nor can it undergo dehydration to a diene.

The dimethylbutenol was passed over alumina and zinc oxide under the experimental conditions and with the results stated in Table I.

TABLE I

REACTION OF Δ^3-2,2-DIMETHYLBUTENOL-1 OVER ALUMINUM AND ZINC OXIDES

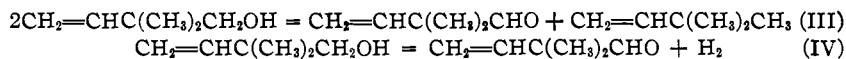|	Catalyst	Temp. °C.	Rate per hour of passage of alcohol and formation of products Alcohol, ml.	Aldehyde, moles	Hydrogen, moles	Gas, ml.	Gas analysis (%) (excluding N_2) CO$_2$	CO	C_nH_{2n}	O$_2$	H$_2$
1	Alumina	300	19.3	0.030	0.0001	174	11.5	41.2	25.3	3.8	1.1
2	Zinc oxide	300	20.5	.019	.0181	705	14.1	10.1	13.5	3.2	57.5
3	Zinc oxide	330	19.4	.029	.0405	1652	8.1	18.0	18.3	2.0	55.0
4	Zinc oxide	330	16.0	.024	.0434	1360	3.5	19.9	7.0	...	71.5

The weight of aldehyde given in Expt. 4 was obtained by fractionation, while the amounts given in Expts. 1, 2 and 3 were obtained by weighing the amount of p-nitrophenylhydrazone formed as previously described. The same aldehyde, i. e., Δ^3,2,2-dimethylbutenol-1, $CH_2{=}CHC(CH_3)_2$-CHO, was produced over both zinc and aluminum oxides, as was evidenced

[1] Weston and Adkins, THIS JOURNAL, 50, 1930 (1928); 51, 2430 (1929).

by the melting points of mixtures of the semicarbazones of the product from different experiments. There was also produced over both catalysts an unsaturated hydrocarbon boiling at 37–39°. This hydrocarbon was apparently 3,3-dimethylbutene-1.

The behavior of the dimethylbutenol differed over the two catalysts in that practically no hydrogen was produced over alumina, while over zinc oxide there was a considerable amount of dehydrogenation.

It is obvious from the above facts that over alumina, aldehyde was produced only through the autooxidation–reduction of the unsaturated alcohol (Equation III) while over zinc oxide this reaction occurred along with the dehydrogenation reaction (Equation IV) common to primary and secondary alcohols.

$$2CH_2=CHC(CH_3)_2CH_2OH = CH_2=CHC(CH_3)_2CHO + CH_2=CHC(CH_3)_2CH_3 \quad (III)$$
$$CH_2=CHC(CH_3)_2CH_2OH = CH_2=CHC(CH_3)_2CHO + H_2 \quad (IV)$$

This is in marked contrast to the behavior of allyl alcohol over zinc oxide, which results in only a small amount of dehydrogenation but in the formation of large amounts of propionaldehyde according to reactions V and VI.

$$CH_2=CHCH_2OH = CH_2=CHCHO + H_2 \quad (V)$$
$$CH_2=CHCHO + CH_2=CHCH_2OH = CH_3CH_2CHO + CH_2=CHCHO \quad (VI)$$
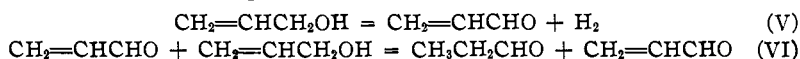
Benzyl alcohol is similar to Δ^3,2,2-dimethylbutenol-1 in that it is a primary alcohol without a hydrogen atom on the 2-carbon atom and with unsaturation in the 3,4-position. When passed over alumina it behaved similarly to the dimethylbutenol in that disproportionation took place with the formation of benzaldehyde and toluene as in Equation VII. The experimental details are given in Table II.
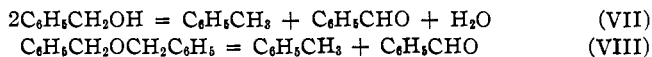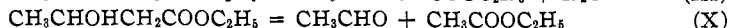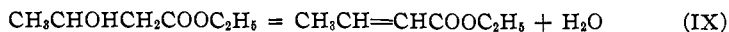
$$2C_6H_5CH_2OH = C_6H_5CH_3 + C_6H_5CHO + H_2O \quad (VII)$$
$$C_6H_5CH_2OCH_2C_6H_5 = C_6H_5CH_3 + C_6H_5CHO \quad (VIII)$$

TABLE II

REACTIONS OF BENZYL ALCOHOL AND OF DIBENZYL ETHER OVER ALUMINA

Substance	Temp., °C.	Ml./hr.	Toluene per hour, g.	Dibenzyl ether, %	Toluene, %	Benzaldehyde, %
Dibenzyl ether	340	22.5	2.93	..	27.0	25.8
Benzyl alcohol	340	21.8	3.15	22.0	32.6	27.6
Benzyl alcohol	340	16.6	2.20	24.0	31.0	31.0
Benzyl alcohol	340	13.5	2.10	25.6	35.0	38.0

It is possible that the auto-oxidation reduction of benzyl alcohol involves the disproportionation of dibenzyl ether formed through the catalytic action of alumina on benzyl alcohol (Equation VIII) as dibenzyl ether is formed in a good yield when benzyl alcohol is passed over alumina. Toluene and benzaldehyde are formed in similar amounts irrespective of whether the alcohol or the ether is passed over the catalyst. It is reported that dibenzyl ether disproportionates under the influence of high temperatures but under the experimental conditions used in this investigation the

amount of disproportionation of the ether was shown to be quite negligible except in contact with alumina.

The catalytic dehydration of a hydroxy ester over alumina is apparently accompanied by a considerable amount of disproportionation and rupture of the molecule. When the ethyl ester of β-hydroxybutyric acid was passed over alumina the dehydration (Equation IX) was accompanied by an almost equal amount of disproportionation (equation X).

$$CH_3CHOHCH_2COOC_2H_5 = CH_3CH=CHCOOC_2H_5 + H_2O \qquad (IX)$$
$$CH_3CHOHCH_2COOC_2H_5 = CH_3CHO + CH_3COOC_2H_5 \qquad (X)$$

A summary of the experimental results is given in Table III.

TABLE III

REACTION OF ETHYL β-HYDROXYBUTYRATE OVER ALUMINA

	325°	325°	325°	350°
Temperature	325°	325°	325°	350°
Rate of passage of hydroxy ester, ml./hr.	10	17.7	26	20
Percentage split to acetaldehyde and ethyl acetate	26.4	24.2	19.2	29.3
Ethyl crotonate, %	35.2	32.6	26.2	33.3
Recovered ethyl β-hydroxybutyrate, %	25.4	33.4	45.5	22.0

The disproportionation of the hydroxy ester is not a reaction of ethyl crotonate, for that ester is quite stable over alumina at 325°. A reaction takes place exclusively in the sense of Equation X if the α,α-dimethyl-β-hydroxy ester is used. The yield of ethyl isobutyrate was 35.7% when 15.5 ml. of the hydroxy ester was passed over 2.5 g. of alumina at 325° for one hour. Ethyl 2-methyl-2-ethyl-3-hydroxybutyrate also reacts over alumina in the sense of Equation X. The yield of ethyl 2-methyl-butyrate was 61% when 12.5 g. of the hydroxy ester was passed over 2.5 g. of alumina at 315° for one hour.

It has been shown that alumina catalyzes several types of reactions in hydroxy compounds: (1) dehydration of alcohols to ethers; (2) dehydration of alcohols and hydroxy esters to alkenes or unsaturated esters; (3) reduction of 2,3-unsaturated aldehydes and oxidation of alcohols; (4) intramolecular rearrangement of hydrogen in 2,3-unsaturated alcohols; (5) disproportionation without rupture of the molecule of alcohols having no hydrogen on the carbon atom alpha to the carbinol group; (6) disproportionation with rupture of the molecule of the ether of an alcohol of the type noted above; (7) disproportionation with rupture of the molecule of hydroxy esters, especially if there are substituents on the carbon adjacent to the carbinol group.

It is clear from a consideration of the diversity of the reactions noted above that it is a mistake to describe alumina as a dehydrating catalyst, for this characterization rests upon the chance that chemists first and most conveniently tested its activity toward simple saturated alcohols. The fact that water is split out of these simple alcohols should not therefore be

allowed to bulk very large in devising an hypothesis to account for the catalytic activity of the oxide. Since the type of reaction induced varies with the space relationships in the organic molecule, it is reasonable to suppose that space relationships or the surface of different catalysts are factors in the type of reaction catalyzed. For the present it seems unwise to go beyond the conception that alumina activates or labilizes the organic molecule (and in the case of bimolecular reaction, orients molecules in juxtaposition) so that any one of several reactions is possible. The reaction actually resulting then depends upon the chemical and physical characteristics of the organic molecule.

Experimental Part

The data given under Expts. 1, 2 and 3 in Table I were obtained as described in a previous paper.[1] Two ml. of catalyst was used in studying the reactions of the alcohols and ethers while 2.5 ml. was used for the esters. Two and three-tenths grams of an unsaturated hydrocarbon boiling at 38–40° was fractionated out of the condensate from the passage of 15.5 g. of the dimethylbutenol over alumina at 300°. Five grams of the unsaturated hydrocarbon was obtained in three hours forty-four minutes (Expt. 4, Table I) from the alcohol over zinc oxide at 330°. On drying and redistillation it boiled at 37–39°. In all probability it is 3,3-dimethylbutene-1. Formin and Lochanski reported this hexylene to boil at 41.2° at 760 mm.[2] It was converted to the dibromide derivative, which boiled at 57–57.5° at 17 mm.; however, the quantities were too small to purify for a proper analysis. The yield of aldehyde in Expt. 4 was 9 g. and on redistillation and drying it boiled at 98.5 to 99.5°; d_{25}^{25} 0.8184; n_D 1.4072 at 25°. *Molecular refraction.* Calcd. for 2,2-dimethyl-Δ^3-butenal: 29.45. Found: 29.51. The aldehyde was converted to the semicarbazone derivative, which after two recrystallizations melted at 158.5–160.5° and was not changed by a third recrystallization.

Anal. Calcd. for $C_7H_{13}ON_3$: C, 54.19; H, 8.39. Found: C, 53.88, 53.97; H, 8.57, 8.55.

It was demonstrated that the aldehyde produced over alumina was identical with the aldehyde produced over zinc oxide by a mixed melting point of the semicarbazone derivatives, which was 158.5–160°. The melting point was 157.5–159° for the derivative of the aldehyde produced by alumina.

The toluene and benzaldehyde (Table II) from benzyl alcohol and dibenzyl ether were characterized by the formation of 2,4-dinitrotoluene and the phenylhydrazone of benzaldehyde. The percentage split to ethyl acetate and acetaldehyde (Table III) was determined by saponifying the 25 to 95° fraction of the condensate and titrating the acetic acid formed. The percentages of ethyl crotonate and percentages of recovered ethyl β-hydroxybutyrate were calculated from the results of the fractionation of the condensate. The acetaldehyde was characterized by the p-nitrophenylhydrazone, and the acetic acid by the p-toluidide.

The preparation of Δ^3,2,2-dimethylbutenol-1 is described in the preceding paper.[3]

Ethyl 2-methyl-2-ethyl-3-hydroxybutyrate was obtained by the reduction of ethyl α-methyl-α-ethylacetoacetate with a nickel catalyst in 87% yield;[4] b. p. 97–98° at 14.5 mm.; d_{25}^{25} 0.9775; n_D 1.4340 at 25°. *Molecular Refraction.* Calcd., 46.94. Found, 46.39.

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[2] Formin and Lochanski, *Ber.*, **46**, 244, 1219 (1913).

[3] Folkers and Adkins, THIS JOURNAL, **53**, 1416 (1931).

[4] Adkins, Connor and Cramer, *ibid.*, **52**, 5195 (1930).

Anal. Calcd. for C₉H₁₈O₃: C, 62.02; H, 10.42. Found: C, 61.64, 61.49. H, 10.42, 10.40.

Ethyl 2,2-dimethyl-3-hydroxybutyrate was obtained by the reduction with a nickel catalyst of ethyl dimethylacetoacetate. Yields of 87–88% of the product were obtained which boiled from 94–95° at 21 mm.[4]

Ethyl Δ³,2,2-dimethylbutyrate was obtained by the dehydration of ethyl 2,2-dimethyl-3-hydroxybutyrate with phosphorus pentoxide: b. p. 139–141°; yields, 74–80%.[5]

Catalysts.—Two hundred grams of aluminum nitrate was dissolved in two liters of cold water and concentrated ammonium hydroxide added with stirring until slightly ammoniacal. The precipitate was then filtered with suction and added to two liters of water, and stirred well to dissolve any soluble salt. The precipitate was filtered and added to one liter of water and well stirred again. After filtration the precipitate was dried in an oven at 125°. The alumina was then pulverized in a mortar and again placed in the oven until thoroughly dry. While it was still hot from the oven it was plunged into one liter of water. At this point some was lost due to the alumina forming a non-filterable suspension. After filtration, the oven drying at 125° was repeated. The dry powder was then pressed into pill form. This alumina had fair activity which was increased by heating at 400° for four hours. The zinc oxide was the same as that prepared by Weston from zinc oxalate.

Summary

Alumina does not catalyze (as with allyl alcohol) the reduction of the alkene linkage in Δ³,2,2-dimethylbutenol-1 either through the rearrangement of hydrogen from the carbinol group of the same molecule or through the oxidation of a second molecule of the alcohol to an unsaturated aldehyde. Zinc oxide catalyzes the dehydrogenation of the alcohol to the aldehyde. Alumina and zinc oxide catalyze the autooxidation–reduction of Δ³,2,2-dimethylbutenol-1 with the formation of an unsaturated aldehyde and unsaturated hydrocarbon. Benzyl alcohol and dibenzyl ether disproportionate in an analogous fashion. Alumina catalyzes the disproportionation of β-hydroxybutyric ester, and α,α-dialkyl-β-hydroxybutyric esters with the formation of acetaldehyde and a saturated ester.

MADISON, WISCONSIN

[5] Courtot, *Bull. soc. chim.*, **35**, 111–113 (1906).