77. *The Catalytic Dehydrogenation of Alcohols to Aldehydes in the Presence of Air.*

By R. Ronald Davies and Herbert H. Hodgson.

The catalytic dehydrogenation of butyl, dodecyl, and benzyl alcohols mixed with air has been studied in the vapour phase; the optimum yield of aldehyde has been found to depend on a specific air/alcohol ratio for each alcohol. The aldehyde production efficiencies of four varieties of catalyst have been compared. The amount of oxygen consumed is less than that demanded by theory for external oxidation, so dehydrogenation must have occurred.

THE best and probably the most general method for conversion of alcohols into aldehydes is catalytic dehydrogenation, since direct oxidation, *e.g.*, by chromic acid, although fairly successful with aliphatic alcohols of low molecular weight, gives complex mixtures of aldehydes, acids, esters, and acetals with higher alcohols. Such complexity arises even with *n*-butyl alcohol, which is oxidised by chromic acid mainly to *n*-butyl butyrate (cf. Weizmann and Gerrard, J., 1920, **117**, 328). Sabatier and Senderens (*Compt. rend.*, 1903, **136**, 738, 921, 983) found that if alcohols were passed in the vapour phase over reduced copper at 300°, hydrogen was released and the corresponding aldehyde formed. This method was developed by Bouveault (*Bull. Soc. chim.*, 1908, **3**, 50, 119) into a continuous process, the catalyst being formed by reduction at 300° of copper hydroxide precipitated on copper gauze. Weizmann and Gerrard (*loc. cit.*) obtained a theoretical yield of *n*-butaldehyde from *n*-butyl alcohol by the Bouveault procedure, and Moureu and Mignonac (*Compt. rend.*, 1920, **170**, 258) minimised the reversible reduction back to alcohol by the liberated hydrogen by using a copper–silver catalyst [cf. also Aleksandrova, *J. Appl. Chem. U.S.S.R.*, 1937, **10**, 105 (*Chem. Abs.*, 1937, 4206)].

The present investigation was designed to ascertain the general applicability of the above process modified by admixture of the alcohol with air; butyl, dodecyl, and benzyl alcohols were selected for the purpose, and the efficiencies of four varieties of catalyst have been compared. The experimental data indicated that dehydrogenation was best effected by a copper–silver catalyst on pumice and within a temperature range of 300—350°. A definite air/alcohol ratio appears to be specific for a maximum yield of aldehyde, the optimum amount of air being in all cases well below the theoretical value for oxidation by the oxygen; *e.g.*, for *n*-butyl alcohol the amount of oxygen consumed was only 13% of the theoretical. Further, the aldehyde produced was comparatively pure, and the main by-product (only present in small quantities) was the corresponding carboxylic acid. This ultimate oxidation to acid was less pronounced with the saturated aliphatic alcohols than with benzyl alcohol. When too much oxygen was used (*i.e.*, excess over the particular amount which produced the optimum yield of aldehyde), oxidation proceeded to the carboxylic acid even though the total oxygen consumed from the air was still less than theory demanded for external oxidation. It would appear, therefore, that the mechanism is twofold, *viz.*, catalytic oxidation of the alcohol by the air alongside catalytic dehydrogenation of the alcohol to aldehyde and hydrogen. It is suggested that one function of the atmospheric oxygen is to remove hydrogen adsorbed at the surface of the catalyst.

EXPERIMENTAL.

Apparatus.—A 250-c.c. bolt-head flask, heated in an oil-bath, was fitted with a bung having 3 apertures through which passed an air inlet connected with a flow-meter (capable of measuring air velocities of 0—3000 c.c./min.), a dropping funnel, and a connection to a copper tube (1 m. long and 2 cm. in diam.) containing the catalyst, through which the reacting gases passed, *via* a glass tube, to a condenser attached to a distillation flask which could be connected directly to a vacuum pump if required. The copper tube was provided with thermometers at each end.

Preparation of the Four Catalysts used for Comparison Purposes.—(a) *Copper on kieselguhr.* The kieselguhr (50 g.) was prepared and impregnated as described in the preceding paper.

(b) *Copper–silver on kieselguhr.* The copper–kieselguhr above was immersed in 10 times its weight of 10% ammoniacal silver nitrate, removed, washed free from ammonia with water, and dried in a stream of hydrogen.

(c) *Copper–silver on pumice.* The procedure was as for (a) with pumice (lumps of *ca.* 0·2 cm. diam.) instead of kieselguhr, and silver was deposited as for (b).

(d) *Silver on copper gauze.* The copper gauze (100 mesh) was cleaned by 10 mins.' immersion in 10% ammoniacal silver nitrate, washed, and dried as under (b).

Method of Working.—The oil-bath for heating the flask was set at a temperature 20° higher than the b. p. of the alcohol to be hydrogenated, which was added from the graduated dropping funnel at a predetermined rate, the air current being also regulated by the flowmeter, and the catalyst maintained at a given temperature. When the reaction had commenced in the catalyst tube, very little additional heat was required, but regulation of the heating to secure the fixed temperature was easily effected by gas burners.

Dehydration of Butyl Alcohol.—The results are in Table I, fuller details of expts. 11, 18, and 19, which were conducted with 200 g. of *n*-butyl alcohol, being given in Table II.

For butyl alcohol at atmospheric pressure and with a flow ratio of 1000 c.c. of air to 10 c.c. of alcohol per min., there is little to choose between the copper–silver on pumice and the silver on copper gauze catalysts, whereas the copper–silver kieselguhr catalyst gave poor results, a circumstance attributed to alteration of gas ratio by partial choking. Copper gauze alone gave reasonable yields of aldehyde, although they were slightly contaminated with butyric acid. The copper–silver catalysts which had been deactivated by prolonged exposure to atmospheric conditions were readily re-activated by renewed treatment with ammoniacal silver nitrate.

Optimum conditions for aldehyde formation at atmospheric pressure. These are indicated by expts. 11, 18, and 19, where the products contained only traces of *n*-butyric acid, *viz.*, by the use of a copper–silver catalyst on pumice at 350° with an air/alcohol ratio of 500/5 c.c. per min. Increase in the proportion of air or replacement of the copper–silver catalyst by copper resulted in an increase in the amount of *n*-butyric acid produced, whereas decrease in the proportion of air decreased the conversion.

Method of analysis (also employed for the dodecyl and *n*-butyl alcohol experiments). The total condensate from each experiment was dissolved in ether, separated from water, and dried over sodium sulphate, the ether removed, and the residual oil weighed. The oil (20 g.) was dissolved in ether (100 c.c.) and shaken three times with 10% aqueous sodium bisulphite (3 × 100 c.c.), the ethereal part being used for the estimations. (*a*) In one half, acid was determined by direct titration with 0·2N-alcoholic potassium hydroxide (phenolphthalein indicator) and (*b*) ester by adding to the titrated solution 20 c.c. of 0·2N-alcoholic potassium hydroxide, boiling the mixture under reflux for 2 hours, and subsequently back-titrating it with 0·2N-sulphuric acid, the amount of ester being calculated as *n*-butyl butyrate. In the other half, (*c*) unchanged alcohol was determined by evaporating the solution at 50°, and estimating the alcohol content in the residue by acetylation, followed by determination of the saponification value, allowance being made for the amount of ester present. (*d*) The above bisulphite solution was heated with sulphuric acid for 1 hour under reflux, the liberated aldehyde extracted by ether, and estimated by Stillmann and Reed's method (*Perfume and Essential Oil Record*, 1932, 279).

Identification of the aldehyde formed. The oil (470 g.) from expts. 11, 18, and 19, remaining after analysis, was shaken

TABLE I.

Effect of catalyst, air/alcohol ratio, and temperature on the yield of n-*butaldehyde.*

Expt.	Air vel., c.c./min.	Alcohol vel., c.c./min.	Catalyst.	Temp.	Conversion, %.	Yield after allowance for recovery of alcohol, %.
1	500	5	(a)	300°	63	86
2	1000	5	,,	300	68	83·5
3	2000	10	,,	300	73	83
4	2000	10	,,	350	69	72 *
5	2000	10	(b)	300	64	86
6	500	5	,,	250	52	87
7	1000	5	,,	350	86	82
8	1000	5	(c)	300	69	89
9	1000	5	,,	350	87	88
10	1000	5	,,	400	82	84
11	500	5	,,	350	89	96
12	500	5	Cu	350	73	87
13	1000	5	,,	350	81	84
14	500	5	,,	300	67	85·6
15	500	5	(d)	350	88	92
16	1000	5	,,	350	89	86
17	500	5	,,	300	72	93
18	500	5	(c)	350	90	94 †
19	500	5	,,	350	88	97 †

* Choking was troublesome in all experiments with kieselguhr.
† Expt. 11 was repeated with the same catalyst revivified.

TABLE II.

Expt.	Weight of oil, g.	Aldehyde, g.	Aldehyde, %.	Alcohol recovered, g.	Alcohol recovered, %.	Conversion, %.	Yields, %. Aldehyde.	Ester.	Acid.
11	192	166	86·5	22	11·5	89	96	0·5	—
18	189	164·5	87·0	20	10·6	90	94	1·2	0·2
19	194	166	85·5	24	12·4	88	97	0·3	0·6

with 3 portions of 10% sodium bisulphite solution (total 500 c.c.). The combined bisulphite liquors were extracted twice with ether (600 c.c.), the aqueous solution hydrolysed with hydrochloric acid, the aldehyde extracted therefrom with ether, and the ether evaporated. This left 394 g. of oil, which, after addition of sodium carbonate (2 g.), was fractionated with a 2′ column packed with ¼″ Lessing rings for the lower 20″; 3 fractions were coolected at 764 mm., *viz.*, up to 70° (30 g.), b. p. 70—73° (326 g.), and b. p. 78—90° (20 g.). The middle fraction had $n_D^{20°}$ 1·3844, $d_4^{20°}$ 0·8152, and was *n*-butaldehyde ($n_D^{20°}$ 1·3843, $d_4^{20°}$ 0·817, b. p. 74°/760 mm.).

Dehydrogenation of Dodecyl Alcohol (*setting point*, 22°).—The results are in Table III, 200 g. of the alcohol and catalyst

TABLE III.

Expt.	Air vel., c.c./min.	Alcohol vel., c.c./min.	Temp.	Pressure, mm.	Alcohol consumed, %.	Weight of product, g.	Aldehyde formed, %.	Acid, %.
1	500	5	350°	760	93	193	79	12·2
2	500	5	350	100	91	195	81	8·3
3	500	5	350	20	94	192	76	16·3
4	250	5	350	100	86	194	88	—
5	250	5	250	100	63	198	82	—
6	200	5	300	100	88·5	191	85	2·1

(c) being used. The optimum conditions, which afforded a yield of 88%, were therefore : alcohol velocity, 5 c.c./min.; air velocity, 250 c.c./min.; temperature, 300—350°; pressure, 100 mm. The increased proportion of lauric acid, compared with that of *n*-butyric acid in the dehydrogenation of *n*-butyl alcohol, is noteworthy, and the reaction appeared to be less exothermic.

Dehydrogenation of Benzyl Alcohol.—200 G. were used, with catalyst (c) and atmospheric pressure, since no advantage accrued from working at lower pressures. The results (below) show that the optimum conditions (76·5% yield) are a

TABLE IV.

Expt.	Air vel., c.c./min.	Alcohol vel., c.c./min.	Temp.	Alcohol consumed, %.	Weight of product, g.	Aldehyde formed, %.	Acid, %.
1	500	5	300°	63	200	61·5	16·0
2	750	5	300	77	197	76·6	12·2
3	1000	5	300	71	198	70·6	17·0
4	750	5	350	76	196	76·0	10·1

ratio of 750 c.c. air/5 c.c. alcohol per min. at 300—350°. The yields of aldehydes in all cases are below those for the aliphatic alcohols (above), and an appreciable amount of benzoic acid was formed, the reaction being less exothermic than for *n*-butyl alcohol.

TECHNICAL COLLEGE, HUDDERSFIELD.

[*Received, April 6th,* 1943].