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## VAPOUR PHASE, CATALYSED REACTIONS

### INTRODUCTION

THE REACTANTS are passed as vapour through a hot tube containing a catalyst, and the products are condensed or scrubbed from the issuing gas. Rate of vapour flow, pressure, temperature, and time of contact with the catalyst are readily controllable. Because the method is especially suitable for large-scale and continuous operation, it has become increasingly important industrially.

Amongst the many industrial organic chemical processes carried out catalytically in the vapour phase are: cracking of higher crude petroleum fractions to olefines and low molecular weight branched-chain paraffins, and the cracking of natural gas to  $C_2$ - $C_4$  olefines, at  $400^\circ$  over alumina-silica; polymerization of olefines to high octane petroleum at  $200^\circ/200$  lb./in.<sup>2</sup> over supported phosphoric acid; dehydrogenation of  $C_6$  and higher paraffins to benzenoid hydrocarbons (e.g. heptane  $\rightarrow$  toluene) at  $400^\circ$  over copper chromite or zinc oxide-alumina; production of methanol from water gas at  $200$ - $450^\circ/50$ - $350$  atm over zinc chromite; oxidation of ethanol to acetaldehyde with air at  $300^\circ$  over copper gauze; production of acetone from ethanol and steam at  $450^\circ$  over reduced iron oxide-lime.

In the laboratory, there are many preparative applications of the vapour phase catalytic method, e.g. the preparation<sup>1</sup> of aldehydes and ketones by dehydrogenation of primary and secondary alcohols over copper chromite at  $320^\circ$  (see below); the dehydration<sup>2</sup> at  $350^\circ$  of cyclohexanols to cyclohexenes over basic aluminium phosphate; the preparation of dihydropyran from tetrahydrofurfuryl alcohol at  $330^\circ$  over alumina<sup>3</sup>; the cracking of acetates to olefines at  $500^\circ$  over silica<sup>4</sup>; and the preparation of nitriles from carboxylic acids and ammonia at  $400^\circ$  over basic aluminium phosphate<sup>5</sup> (one example is given on p 162). Where applicable, the vapour phase catalytic method is undoubtedly superior to the more conventional laboratory procedures.

# DEHYDROGENATION OF ALCOHOLS

## REFERENCES

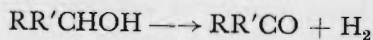
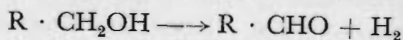
### General:

- EMMETT, *Catalysis*, Reinhold Publishing Corp., New York: especially especially 1956, Vol. 4; 1958, Vol. 6; 1960, Vol. 7; see also succeeding volumes.
- FRANKENBURG, KOMAREWSKY and RIDEAL, *Advances in Catalysis and Related Subjects*, Academic Press Inc., New York: especially 1956, Vol. 4; 1958, Vol. 6; 1960, Vol. 7; see also succeeding volumes.
- KOMAREWSKY and RIESZ, *Catalytic Reactions*, in *Technique of Organic Chemistry* (ed. Weissberger), Interscience Publishers Inc., New York, 1956, Vol. II.

### Particular:

- <sup>1</sup> ADKINS, KOMMES, STRUSS and DASLER, *F. Amer. chem. Soc.*, 1933, **55**, 2992.
- <sup>2</sup> cf. *French Patent No. 679,997* (1928); *British Patent No. 627,453* (1949).
- <sup>3</sup> *Org. Synth.*, 1943, **23**, 25.
- <sup>4</sup> BURNS, JONES and RITCHIE, *J. chem. Soc.*, **1935**, 400.
- <sup>5</sup> cf. *British Patent No. 451,594* (1936); *U.S. Patent No. 2,200,734* (1940).

### (i) DEHYDROGENATION OF ALCOHOLS OVER COPPER CHROMITE AT 320°



### *Catalyst*

Dissolve copper nitrate (45 g) in a hot, stirred solution of barium nitrate (5 g) in water (150 c.c.), and to the hot solution add a warm solution of ammonium dichromate (25 g) in a mixture of water (100 c.c.) and concentrated aqueous ammonia (35 c.c.). Stir the mixture for a few minutes and allow it to cool. Collect the precipitate on a 7-cm Buchner filter, wash it with water (200 c.c.), transfer it to a beaker and mix it with sufficient water to form a thin cream. Add pumice (150 g; 3-8 mesh), stir the mixture until the pumice is uniformly coated, and then transfer the mass to a clean iron pan. Stir the mass with a glass rod, and heat it gently to expel the water. Soon, the coated granules of

pumice no longer adhere to one another. Continue to stir and heat the mixture until it is uniformly black.

It is unnecessary in the present experiment to pretreat the catalyst with hydrogen, although this increases its efficiency. The operation needs careful control to prevent too extensive reduction of the cupric oxide.

### *Apparatus*

The copper reaction tube (30 × 1 in.) (see *Figure 76*) is heated electrically by an asbestos-insulated winding capable of giving temperatures up to 450°. Control is by a variable transformer. The turns of the heater winding are so spaced that at ca. 300°, the temperature is uniform along its length. There is a narrow glass tube down the centre of the reaction tube for a thermocouple junction connected to a direct reading indicator (Foster Instrument Co. Ltd., Letchworth, Herts).

### *Procedure*

Push a plug of glass-wool down the copper tube to *f* (*Figure 76*). Insert from the end *d* the thermocouple tube *e* and the 360° thermometer, and work them through the plug at *f*. The bulb of the thermometer should reach 2–5 cm into the catalyst space below the plug at *f*. Invert the copper tube, pour the copper chromite catalyst in (from *h*) and tap the tube gently. Plug the tube at *g* with glass-wool and return the tube to its upright position. Connect the Vigreux column condenser and receiver *a*, as shown.

Switch on the reaction tube heater. Clip the tube *e* and draw a *very slow* stream of air through the catalyst by connecting the receiver *a* to a water pump. This process completes the ignition of the catalyst. (Too rapid a stream of air inactivates the catalyst.) When the temperature in the reaction tube at *f* reaches 320° (as shown by the thermometer), remove the clip at *e* and disconnect the pump from the receiver *a*. Then attach the boiler *i*, containing the alcohol (any lower primary or secondary carbinol) (100 c.c.) and some porous chips. Place a heating mantle on a laboratory jack underneath the boiler and raise the mantle into position. Switch on the heating mantle (controlled by a variable transformer) and connect the receiver *a* to the inlet of a Drechsel bottle which contains water. To obtain smooth dehydrogenation of the alcohol, as indicated by a steady and fairly rapid evolution of hydrogen, adjust the heat inputs to the boiler and to the reaction tube, so that:

- (1) The temperature of the hottest zone in the tube is 320–330° (above 350°, dehydration of the alcohol sets in);
- (2) The temperature at *b* does not rise above the boiling point of the aldehyde or ketone being formed;
- (3) The rate of collection of distillate does not exceed 1 drop/second.

## DEHYDROGENATION OF ALCOHOLS

Investigate the temperature along the reaction tube with the movable thermocouple: the reaction is strongly endothermic. Measure the rate of hydrogen evolution by collecting the gas over water.

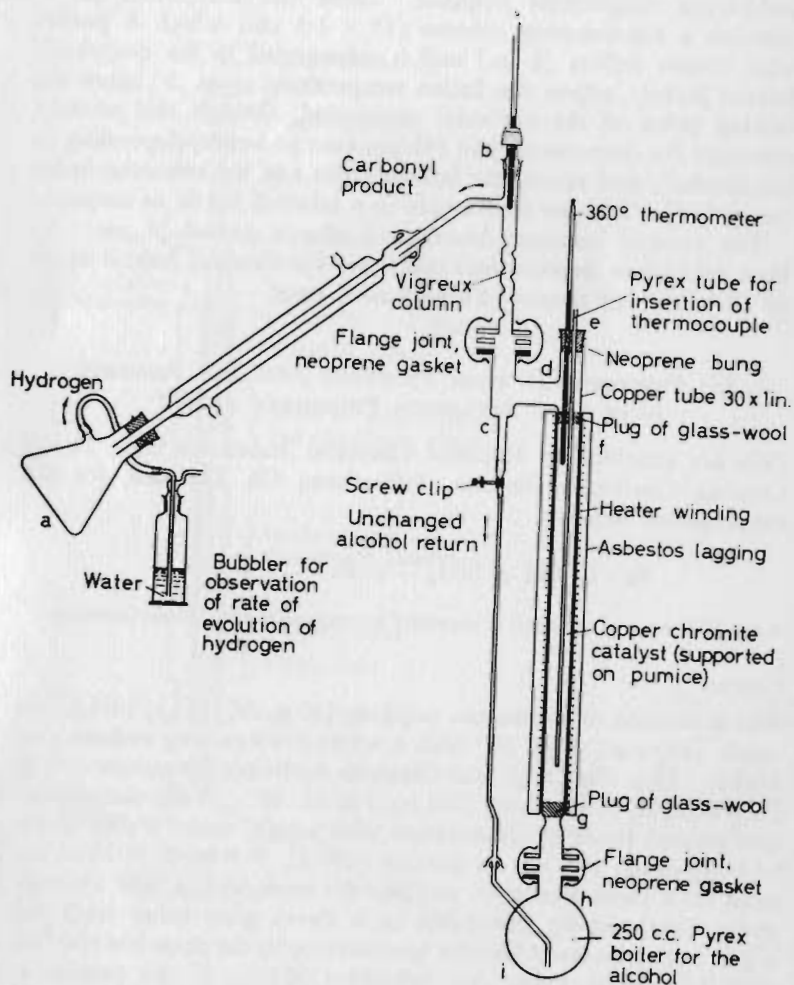


Figure 76. Apparatus for the dehydrogenation of primary and secondary alcohols over copper chromite

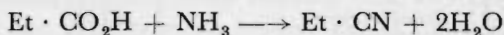
water in an inverted measuring cylinder for 5-minute periods: this gives the rate of dehydrogenation.

When the volume of alcohol in the boiler *i* has fallen to *ca.* 20 c.c., disconnect the Drechsel bottle at *a*, and switch off the heaters. Measure the volume of the unused alcohol. Dry the distillate, which consists of carbonyl compound and a little water, with anhydrous magnesium sulphate. Distil the compound slowly through a fractionating column (15 × 1.5 cm) which is packed with Fenske helices ( $\frac{1}{8}$  in.) and is surrounded by an electrically heated jacket: adjust the jacket temperature to *ca.* 5° below the boiling point of the carbonyl compound. Weigh the product, calculate the conversion yield (45 per cent or better, depending on the alcohol), and record the boiling point and the refractive index (see p 111). Transfer the sample to a labelled bottle or ampoule.

The catalyst becomes deactivated after a period of use. To burn off carbon deposits and reactivate the catalyst, heat it *in situ* at 320° in a *slow* stream of air for *ca.* 1 hour.

(ii) PROPIONITRILE FROM PROPIONIC ACID AND AMMONIA  
OVER BASIC ALUMINIUM PHOSPHATE AT 400°

(We are indebted to Imperial Chemical Industries Ltd., Heavy Organic Chemicals Division, Billingham, Co. Durham, for the experimental details.)



A fourfold excess of ammonia is necessary to suppress diethyl ketone formation.

*Catalyst*

Mix a solution of aluminium sulphate [40 g,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ] in water (350 c.c.) at *ca.* 30° with a solution containing sodium carbonate (13 g,  $\text{Na}_2\text{CO}_3$ ) and disodium hydrogen phosphate (14 g,  $\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ ) in water (300 c.c.) at *ca.* 40°. Wash the precipitate several times by decantation with water, make a thin slurry of it in water, and stir in pumice (200 g; 3–8 mesh). Heat the mass on a clean iron tray, and stir the mass with a 500° thermometer (enclosed for protection in a Pyrex glass tube) until the water has evaporated and the temperature in the mass has reached 400° [*cf.* *British Patent No. 649,980* (1951)]. If the pumice is omitted, the calcined, powdered catalyst, mixed with several per cent of graphite, can be pelleted ( $\frac{3}{16} \times \frac{1}{8}$  in. diameter.)

## PROPIONITRILE FROM PROPIONIC ACID

*Apparatus (see Figure 77)*

The silica reaction tube ( $38 \times 1$  in. internal diameter, satin finish but with the top 7 in. and the side tubes in transparent silica) (Thermal Syndicate Ltd., London)

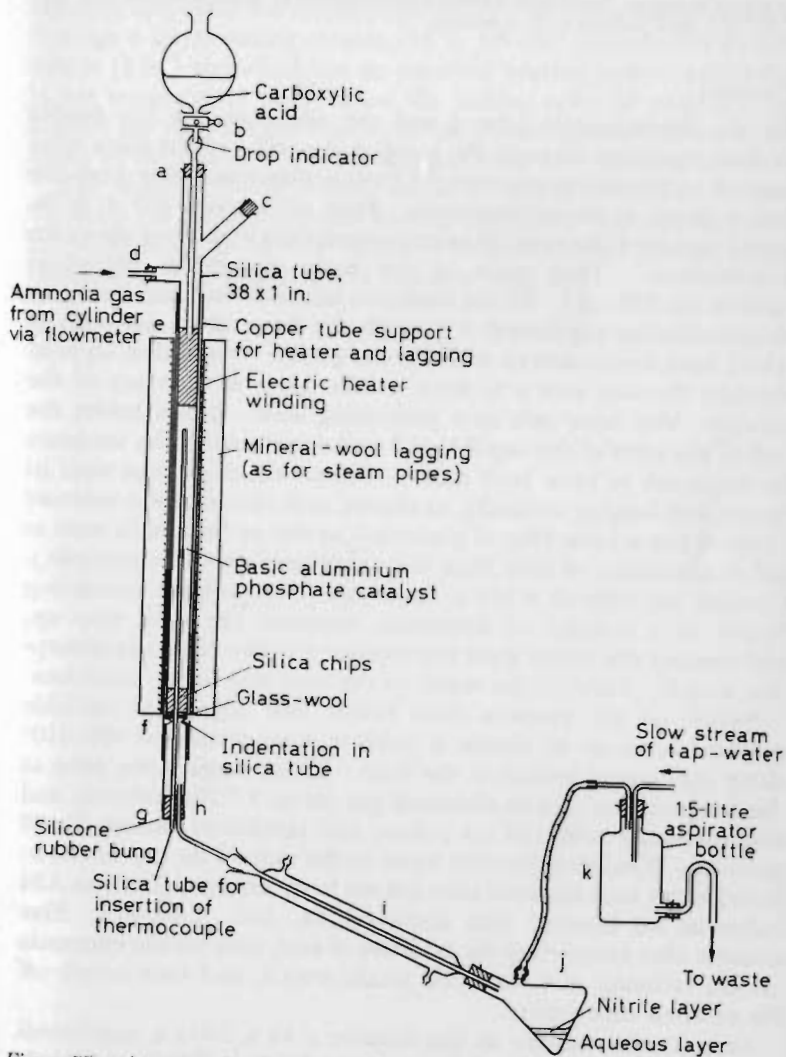


Figure 77. Apparatus for the vapour phase conversion of carboxylic acids to nitriles



## VAPOUR PHASE, CATALYSED REACTIONS

is surrounded for a length of 30 in. by a close-fitting copper tube which carries an electrical heater capable of giving temperatures up to 600°; control is by a variable transformer. The asbestos-insulated winding covers the middle 24 in. of the copper tube and has the turns more closely spaced towards the ends: with this arrangement, the heat input along the length of the catalyst (21 in.) is uniform. The temperature of the catalyst is measured with a (stainless steel sheathed) thermocouple inserted down a narrow, central silica tube (20 in. long). The bung at *h* is of neoprene (Baird and Tatlock Ltd., London) or silicone rubber (e.g. type S.R. 70; Esco Rubber Ltd., London).

### *Procedure*

Fit the thermocouple tube *g* and the connection to the double surface condenser through the bung at the end *h* of the silica tube, nearest to the indentations at *f*. Push a glass-wool plug from the end *a* down to the indentations. Pour silica chips (30 g;  $\frac{3}{16}$  in. mesh) into the silica tube (from end *a*) to form a 2-in. layer above the indentations. Then pour in the basic aluminium phosphate catalyst (ca. 275 c.c.) Fit the ammonia inlet tube at *d* and the Pyrex drop-indicating tap-funnel *b* through the bung at *a*, the holes of which have been smeared with silicone grease. Pour silica chips in through the side arm *c* to form a 4-in. layer at *e* on top of the catalyst: this layer acts as a preheating zone—it also buries the end of the stem of the tap-funnel *b* and so minimizes the tendency for ammonia to blow back into *b*. Mount the silica tube with its heater and lagging vertically, as shown, and connect the condenser *i* (which has a loose plug of glass-wool at one or both of its ends to aid condensation of mist from the gas stream) and the receiver *j*. Connect the tube at *d* via a flowmeter (or a bubbler containing Nujol) to a cylinder of ammonia, mounted the right way up, and connect the outlet from the receiver *j* to the ammonia-absorption trap *k*. Turn on the water to the trap and to the condenser.

Switch on the reaction tube heater and adjust the variable transformer so as to obtain a uniform temperature of 400–410° along the heated section of the tube. Then, keeping the tube at this temperature, pass in ammonia gas (at ca. 1.7 litre/minute) and add propionic acid (40 c.c.) from the tap-funnel during 30–60 minutes. [Occasionally solid forms in the stem of the tap-funnel *b*: in this event melt the solid with hot air from a blower (Latham AM industrial air blower; Sun Electrical Co. Ltd., London)]. Five minutes after completing the addition of acid, turn off the ammonia (at the cylinder) and the water to the trap *k*, and then switch off the reaction tube heater.

Transfer the mixture in the receiver *j* to a 100-c.c. tap-funnel and reject the lower layer (water containing a little ammonium

#### PROPIONITRILE FROM PROPIONIC ACID

propionate, propionamide, propionitrile and diethyl ketone). Wash the upper layer (propionitrile) twice with an equal volume of a solution of calcium chloride (40 g; anhydrous) in 2N-hydrochloric acid (65 c.c.) and twice with an equal volume of *saturated* sodium carbonate solution. Dry the nitrile with anhydrous calcium chloride and distil the nitrile (b.pt 96–97°) at atmospheric pressure through a fractionating column (15 × 1.5 cm) packed with Fenske helices ( $\frac{1}{8}$  in.) and which has an electrical heating jacket; adjust the jacket temperature to 5° below the boiling point of propionitrile. Record the yield (40 per cent, or better), boiling point and refractive index of the nitrile. Transfer the specimen to a labelled bottle.

The catalyst should remain active for up to 120 hours of use. To burn off carbon deposits and so regenerate the catalyst, heat the catalyst *in situ* at 400° for *ca.* 1 hour in a slow stream of air (connect a filter-pump to the reaction tube at *j*).