Electrocatalytic Hydrogenation of 2-Ethylhexanal, 2-Ethylhex-2-enal, Acetophenone, Benzophenone, Butan-2-one, and Cyclohexanone

By **Giuseppe Filardo,* Mosè Galluzzo, Bruno Giannici,** and **Raffaele Ercoli,** Istituto di Chimica Industriale, Università di Palermo, Italy

Catalytic hydrogenation with molecular hydrogen dissolved under pressure in non-aqueous solutions containing the title compounds is achieved, during electrolysis, by transferring copper from the anode to the cathode. The rate of hydrogenation and yield of conversion depend on the current density and temperature. Suitable choice of these variables allows complete conversion of aldehydes and ketones into primary and secondary alcohols, respectively.

On the borderline between chemical and electrochemical processes of reduction, we report a new technique of electrocatalytic hydrogenation which has been briefly outlined in a previous communication.[1] Electrolysis with bulk copper or nickel anodes of non-aqueous solutions containing an unsaturated substrate, in the presence of hydrogen under pressure, causes, during dissolution and deposition of the metal employed, catalytic activation of the hydrogen which is then added to the unsaturated substrate. This procedure, analogous to the electrochemical preparation of species which catalyse processes such as polymerization,[2,3] oligomerization,[4] carbonylation,[5] or oxidation,[6] may be referred to as electrocatalysis. In fact hydrogenation is achieved by transferring metal from the anode to the cathode, while the catalyst is produced and maintained by the current. This paper reports results obtained with copper anodes which, in the above system, show selective hydrogenation of aldehydes and ketones.

EXPERIMENTAL

Pure-grade acetophenone, cyclohexanone, 2-ethylhexanal, 2-ethylhex-2-enal, and butan-2-one were fractionally distilled and stored in 4A molecular sieves; benzophenone was recrystallized before use. The hydrogen used was >99·9% pure.

Hydrogenation was achieved at 40—80 °C and a hydrogen pressure in the range 10—150 atm. All experiments were carried out in a high-pressure electrolytic cell (capacity 250 cm^3, provided with a magnetically driven stirrer) dipped in an oil thermostat bath; the apparatus has been described previously.[7] Although hydrogenation can be carried out on the pure substrate with acceptable yields, it is better to use a solvent, owing to the decrease in conductance during electrolysis. Pyridine, dimethylformamide, and low-boiling alcohols were used. As a rule solutions were made conducting by means of Bu_4NBr, recrystallized from ethyl acetate and dried *in vacuo* at 80 °C; LiCl or other alkali-metal chlorides, depending on their solubility, were also employed. Cylindrical anodes, with a working surface area of 10 cm^2, and beaker-shaped cathodes, working surface area of 50 cm^2, were made of copper (99·9%); cathodes of graphite or non-reactive metals were also used. Currents in the range 8—150 mA were adopted, using an automatic constant-current power supply with limiting voltage set-point. Normally hydrogenation was complete during electrolysis; a drastic decrease in rate of

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[2] M. Guainazzi, G. Filardo, G. Silvestri, S. Gambino, and R. Ercoli, *J.C.S. Chem. Comm.*, 1973, 138.

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[4] H. Lehmkuhl, W. Leuchte, and E. Janssen, *J. Organometallic Chem.*, 1970, **23**, C30.

[5] T. Inoue and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1965, **38**, 2122.

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H_2 absorption, together with a large decrease in conductivity, occurred at the end of the reaction.

In experiment (2) (Table 1), after distillation of the solution, diphenylmethanol was recovered from the crude product by crystallization from alcoholic solution and identified by means of its i.r. spectrum and melting point. As a rule, in all other experiments, after distillation of the solution under reduced pressure, unidentified viscous products and a distillate, in which the products obtained were identified by gas chromatography, remained. The yield of conversion was calculated as the ratio between the amount of alcohol produced and the substrate (aldehyde or ketone) introduced.

RESULTS AND DISCUSSION

Since activation of molecular hydrogen had previously been achieved, with homogeneous catalysis, by means of copper(I) acetate [8,9] in the hydrogenation of *p*-benzoquinone in quinoline, preliminary experiments were carried out with copper-(I) and -(II) salts (acetates and chlorides) dissolved in aldehydes or ketones at 80 °C and a hydrogen pressure of 150 atm. Lengthy experiments showed that spontaneous hydrogenation does not take place without electrolysis; once the current flowed, after an initial stage without absorption, catalytic hydrogenation was achieved. Absorption of hydrogen did not cease when the current stopped; it continued at a decreased rate, involving greater or smaller amounts of substrate depending on the original current density adopted.

Table 1 summarizes results obtained in hydrogenation of some aldehydes and ketones in butan-2-ol, using tetrabutylammonium bromide as electrolyte. Experiment (5) (Table 1) shows that the olefinic bond reacts partially only if conjugated to a carbonyl group; almost equivalent amounts of 2-ethylhexanol and 2-ethylhex-2-enol were found on hydrogenation of 2-ethylhex-2-enal, but hydrogenation failed with cyclohexene and 2-ethylhexene.

TABLE 1

Electrochemical hydrogenation of some aldehydes and ketones

Expt. no.	Substrate	Amount/g	H_2 Pressure/atm Initial	H_2 Pressure/atm Final	10^{-2} Quantity of current passed / faraday	Anodic loss / g	Product	Yield (% substrate)
(1)	Acetophenone	(10)	135	107	3·5	0·83	Methyl(phenyl)methanol	90
(2)	Benzophenone	(7·5)	100	86	1·1	0·34	Diphenylmethanol	90
(3)	Cyclohexanone	(9·9)	146	112	2·6	0·75	Cyclohexanol	95
(4)	2-Ethylhexanal	(8·2)	148	128	6·3	2·62	2-Ethylhexanol	90
(5)	2-Ethylhex-2-enal	(8)	143	116	5·6	2·61	2-Ethylhex-2-enol and 2-Ethylhexanol	82
(6)	Butan-2-one	(8)	145	107	3·5	1·47	Butan-2-ol	95

Solvent, butan-2-ol (20 g); electrolyte, tetrabutylammonium bromide (1·5 g); 80 °C; current, 100 mA; copper cathode (99·9%, 50 cm²), copper anode (99·9%, 10 cm²).

TABLE 2

Influence of temperature and current density on electrochemical hydrogenation of butan-2-one

Expt. no.	t/°C	Current/ mA	H_2 Pressure/atm Initial	H_2 Pressure/atm Final	10^{-2} Quantity of current passed / faraday	Anodic loss / g	Butan-2-ol yield (% substrate)	Other products
(1)	40	25	130	25	7·3	4·3	98	$C_8H_{16}O$, a pinacol
(2)	40	50	134	34	8·65	3·69	87	$C_8H_{16}O$, a pinacol
(3)	40	100	138	42	10·0	2·05	83	$C_8H_{16}O$, a pinacol
(4) *	80	8	142	130	7·8	5·02	9	
(5) *	80	25	130	116	7·8	4·85	11	
(6)	80	50	145	18	20·3	12·60	99·5	
(7)	80	100	147	26	7·7	3·22	95	$C_8H_{16}O$, a pinacol
(8)	80	150	147	42	6·0	1·88	75	$C_8H_{16}O$, a pinacol
(9) †	80	150	119	102	3·13	1·07	12	$C_8H_{16}O$, a pinacol

Substrate-solvent, butan-2-one (25 g); electrolyte, tetrabutylammonium bromide (1·5 g); copper cathode (99·9%, 50 cm²), copper anode (99·9%, 10 cm²).

* Experiment interrupted after 10% decrease of anodic area. † The cell was filled with hydrogen after interruption of the electrolysis.

Under the conditions adopted for this set of experiments, although yields of conversion were always *ca.* 90%, the relation between electric charge passed and anodic loss depended on the aldehyde or ketone. After electrolysis, both spongy and powdered metallic copper, corresponding within a few percent to the anodic loss, was found at the cathode. The hydrogen pressure, in the range studied, did not affect the rate of hydrogenation; the latter was dependent on the current density and temperature. The effects of these variables on the course of reaction were investigated, with fixed quantities and a standard geometry for the cell, for hydrogenation of butan-2-one; the latter was employed without a solvent since good conductivity during electrolysis was

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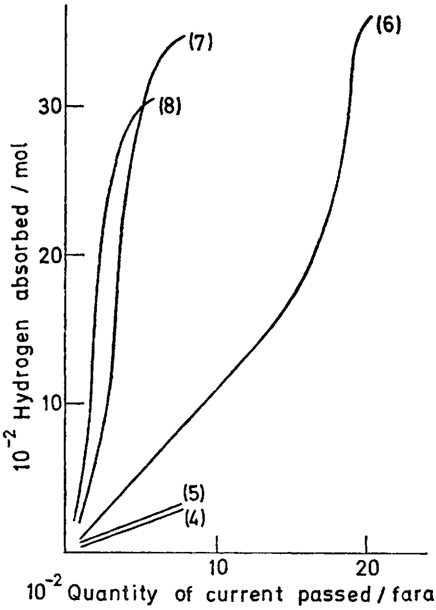
[8] M. Calvin, *J. Amer. Chem. Soc.*, 1939, **61**, 2230.

[9] S. Weller and G. A. Mills, *J. Amer. Chem. Soc.*, 1953, **75**, 769.

obtained. Data at 40 and 80 °C, at different current densities, are summarized in Table 2. The amount of H_2 absorption plotted against the quantity of current passed, for each current density experienced, is shown in the Figure.



Electrochemical hydrogenation of butan-2-one at 80 °C. The plots correspond to expts. (4)—(8) in Table 2

With regard to the experiments at 80 °C, good correspondence between electric charge passed and anodic loss, according to reaction (1), was obtained

$$Cu \longrightarrow Cu^+ + e^- \quad (1)$$

when an initial current density $\leqslant 25$ A m^{-2} was adopted. At the same time, very slow absorption of H_2 occurred (Figure). (These experiments were interrupted when the anodic working area had decreased by 10%.) After distillation of the product solution, apart from butan-2-one, only butan-2-ol was recovered.

The best compromise between rate of hydrogenation and yield was reached if the current density imposed was 2—3% in excess of that required for reaction (1). As shown in Table 2 [expt. (1)], at 40 °C the value of the current density to achieve the above conditions was lower than that at 80 °C. When higher current densities were adopted [expts. (7) and (8)] the weight loss of the copper anode was not in accord with the stoicheiometry (1). Small amounts of Cu^{2+} were found in the residue after distillation, hydrolysed with dilute HCl under a nitrogen atmosphere. Butan-2-one was involved in the electrode reactions since pinacol, 3-methylheptan-5-one, and water were also found in the product solution. However, even if side-reactions involving the substrate are occurring [*ca.* 25% in expt. (8)], the rate of hydrogenation, as gradients of plots of H_2 absorption against quantity of current passed show, increases as the current density increases.

Since from the above it cannot be excluded that the hydrogen is involved in the electrode reactions as a catalytic intermediate, experiments on butan-2-one with a Pt anode were carried out. Hydrogenation did not occur; in the resulting solution, besides condensation products of the substrate, traces of butan-2-ol formed by direct reduction of butan-2-one were found. A comparable amount of butan-2-ol was found in analogous experiments in the absence of hydrogen. When, with both electrodes of copper, the cell was filled with hydrogen after interruption of electrolysis, partial hydrogenation of butan-2-one was achieved [expt. (9), Table 2]. These results suggest that hydrogenation is not directly related to the electrode processes, but depends on species which are electrolytically produced; these, continuously generated by circulation of the current, allow catalytic hydrogenation in the bulk of the solution. When the current density is small enough to impose reaction (1) as the anodic process (in these conditions large amounts of powdered copper are recovered) the hydrogenation rate is very slow. On the other hand, when, at higher current density, both copper-(I) and -(II) ions are present during electrolysis, fast hydrogenation is achieved. One suggestion is that, as with Group VIII metal catalysts,[10] hydrogenation occurs through transfer of hydride ligands to the substrate when co-ordinated to a copper(II) ion.

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