Oxidation of Primary Alcohols to Carboxylic Acids at the Nickel Hydroxide Electrode

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We describe here the smooth oxidation of primary alcohols (**1**) to carboxylic acids (**2**) at the nickel hydroxide anode. For long-chain and certain unsaturated primary alcohols, this method is more convenient and has less limitations than other oxidation methods[1]. For short-chain alcohols, the yields of carboxylic acids are comparable to or even exceed those obtained by the permanganate[2] or nickel peroxide[3] oxidation. With nickel peroxide, the yields decrease with increasing chain length[3] and the nickel peroxide or permanganate oxidation of primary alcohols having chains longer than C_9 has, to our knowledge, not been reported.

The chromate oxidation of unsaturated primary alcohols has to be carried out with the Jones reagent to leave the C=C double bond unaffected and the yields may be un-

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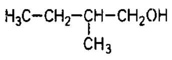
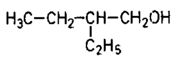
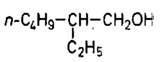
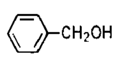
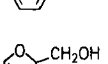
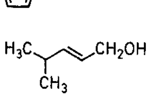
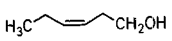
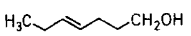
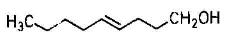
Table. Carboxylic Acids (**2**) from Primary Alcohols (**1**) by Oxidation at the Nickel Hydroxide Anode

1		Electrolyte	Current [A]	Time and temperature		Yield[a] [%]	m.p. or b.p.	
							found	reported
a	n-$C_3H_7-CH_2OH$	A	4	2 h,	70°	85	b.p. 68°/15 torr	b.p. 70.8°/17 torr[10]
		B	0.6	15 h,	25°	92		
b	n-$C_5H_{11}-CH_2OH$	A	4	5 h,	25°	64	b.p. 103°/15 torr	b.p. 102°/15 torr[11]
		B	0.6	15 h,	25°	91		
c	n-$C_6H_{13}-CH_2OH$	A	4	5 h,	25°	84	b.p. 118°/15 torr	b.p. 116°/11 torr[12]
d	n-$C_7H_{15}-CH_2OH$	A	4	6 h,	25°	65	b.p. 136°/15 torr	b.p. 140°/23 torr[12]
		B	0.6	20 h,	25°	49		
		A	4	4 h.	70°	89		
e	n-$C_8H_{17}-CH_2OH$	A	4	7 h,	70°	89	b.p. 145°/15 torr	b.p. 150°/20 torr[12]
		B	0.6	22 h,	25°	13		
f	n-$C_9H_{19}-CH_2OH$	A	4	4 h,	25°	27	m.p. 29–30°	m.p. 31.5°[12]
		B	6	66 h,	25°	12		
		A	4	7 h,	70°	87		
g	n-$C_{11}H_{23}-CH_2OH$	A	4	8 h,	70°	80	m.p. 44°	m.p. 44°[12]
h	n-$C_{17}H_{35}-CH_2OH$	A	4	8 h,	75°	77	m.p. 68–69°	m.p. 69.4°[9]
i	 $H_3C-CH_2-\underset{CH_3}{CH}-CH_2OH$	A	4	3.5 h,	25°		b.p. 81°/15 torr	b.p. 77°/12 torr[12]
j	 $H_3C-CH_2-\underset{C_2H_5}{CH}-CH_2OH$	A	4	3.5 h,	25°	51	b.p. 93°/15 torr	b.p. 90°/13 torr[12]
		A	4	3.5 h,	70°	73		
k	 n-$C_4H_9-\underset{C_2H_5}{CH}-CH_2OH$	A	4	5 h,	25°	31	b.p. 122°/15 torr	b.p. 120°/13 torr[12]
		A	4	7 h,	70°	76		
l		A	4	1.5 h,	25°	86	m.p. 122°	m.p. 122.4°[12]
m		A	4	2 h,	25°	79	m.p. 131–132°	m.p. 133–134°[12]
n		A	4	48 min,	5°	10[b,c]	b.p. 112°/15 torr	b.p. 114–116°/17 torr[13]
o		B	0.6	17 h,	25°	34	b.p. 108°/15 torr	b.p. 102–103°/11 torr[14]
p		A	4	4 h,	25°	82[d]	b.p. 116°/15 torr	b.p. 110–111°/11 torr[14]
q		A	4	8 h,	70°	68[e]	b.p. 130°/15 torr	b.p. 105–106°/1 torr[15]
r	$HC\equiv C-CH_2OH$	A	4	2 h,	5°	51[f]	b.p. 82°/50 torr	b.p. 83–84°/50 torr[12]

[a] Yield of isolated product. The structures of all products were confirmed by their I.R., N.M.R. and mass spectra. Purity was checked using G.L.C. (conditions: 1.70 m glass column, ϕ 2 mm, 5% FFAP/Chromosorb W AW DCMS, 100/120 mesh).

[b] The product was accompanied by considerable amounts of 2-methylpropanoic acid. Additionally, larger amounts of carbon dioxide were formed.

[c] The *trans* configuration is confirmed by the coupling constant ($J=16$ Hz) of the olefinic protons. ^{1}H-N.M.R. (CCl_4): $\delta=1.10$ [d, 6H, $(\underline{H}_3C)_2CH—$]; 2.40–2.70 (m, 1H, $C\underline{H}$); 5.72 (d, 1H, $J=16$ Hz, $—CH{=}C\underline{H}—COOH$); 6.96 (dd, 1H, $J=7$ Hz and 16 Hz, $CH—C\underline{H}{=}CH—$); 11.6 ppm (s, 1H, $—COO\underline{H}$, exchangeable with D_2O).

[d] In collaboration with I. Langer, our institute.

[e] In collaboration with W. Seidel, our institute.

[f] Carried out in a divided cell.

satisfactory due to partial conversion of unreacted alcohol to its ester[4]. Nickel peroxide oxidation of alkenols has only been reported for 2-alkenols[3]; no or only poor oxidation was observed for 4-alkenols[5]. At the nickel hydroxide electrode, however, we oxidized (E)-4-heptenol (**1p**) and (E)-4-nonenol (**1q**) to the carboxylic acids (**2p, q**) in 82 and 68%, respectively.

$$\underset{\mathbf{1}}{R-CH_2-OH} \xrightarrow{\text{electrolysis : } H_2O/NaOH/Ni(OH)_2\text{ anode/steel cathode}} \underset{\mathbf{2}}{R-COOH}$$

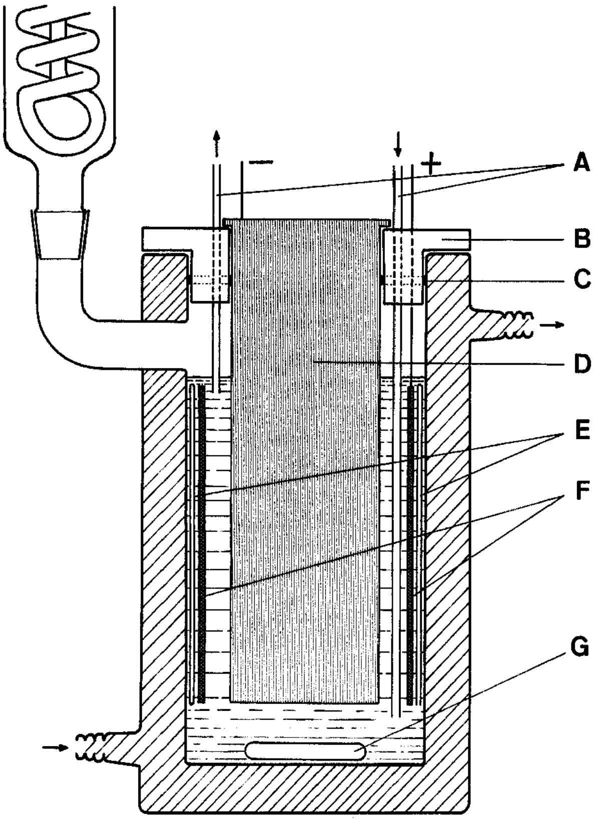
Our electrochemical method for oxidizing primary alcohols has the additional advantage that work up is easy since no conversion products of reagents are formed as is the case in chemical oxidations such as the permanganate, chromate, or nickel peroxide oxidation.

The nickel hydroxide electrode has previously been used for alcohol oxidation by Vertes[6] and by Fleischmann and Pletcher[7]. However these authors were mainly interested in the electroanalytical aspects of the reaction whereas its preparative application remained limited to short-chain and benzylic alcohols and 2,3;4,6-di-O-isopropylidene-L-sorbose.

The oxidation is carried out in *t*-butanol/water/potassium hydroxide (B) or in aqueous sodium hydroxide (A) as electrolytes. Short-chain alcohols are oxidized at room temperature whereas higher temperatures are required for the oxidation of longer-chain alcohols. With saturated alcohols, negligible amounts of C_{n-1} carboxylic acids are formed; in the case of the oxidation of longer-chain alcohols in electrolyte B, the formation of aldol adducts in minor quantities is observed. With 2- and 3-alkenols, the yields are low even at low temperatures and short reaction times whereas good yields are obtained in the case of 4-alkenols. With alkynols, electrolytic hydrogenation of the C≡C triple bond may occur; this drawback is avoided by the use of a divided cell. The yields of carboxylic acids **2a, d, l, m, r** correspond to those reported for the nickel peroxide oxidation[3].

Oxidation of Primary Alcohols at the Nickel Hydroxide Anode:

Apparatus:



A: Inlet and outlet for circulation (pumping) of the electrolyte; **B**: teflon stopper (ϕ 80 mm); **C**: silicon seal; **D**: stainless steel cathode; **E**: glass rods; **F**: nickel net anode; **G**: magnetic stirrer.

The electrolyses are carried out in a double-walled cylindrical glass cell having an electrolyte volume of 300 ml. In order to emulgate the only sparingly water-soluble alcohols, the electrolyte is circulated by pumping (magnetic stirring alone is not sufficient). The anode is a 250 cm^2 nickel net; it is converted to the nickel hydroxide anode before each electrolysis by treatment with a low-frequency alternating current (0.5 Cb/cm^2)[8] in 0.1 normal nickel sulfate/0.1 normal sodium acetate/0.005 normal sodium hydroxide. The cathode is a stainless steel cathode. In certain cases in which cooling or heating is not required, the cell may be replaced by a 600 ml beaker. If a divided cell has to be used, a ceramic diaphragm is placed between anode and cathode.

Conditions of Electrolysis: Electrolyte A: 1 molar aqueous sodium hydroxide; Electrolyte B: *t*-butanol/water (1:1) containing 0.18 mol/l potassium hydroxide. Constant-current electrolysis of 30–40 mmol alcohol at current densities of 2.4 mA/cm^2 (i = 0.6 A) and 16 mA/cm^2 (i = 4 A) and cell voltages of 2.0–2.1 V in an undivided cell.

Stearic Acid (**2h**); *Typical Procedure:* A mixture of octadecanol (**1h**; 8.12 g, 30 mmol) and 1 molar aqueous sodium hydroxide (250 ml) is electrolyzed for 8 h at 75° using a current of 4 A (16 mA/cm^2) and a cell voltage of 2.0 V. The precipitated sodium stearate is then dissolved by the addition of *t*-butanol (20 ml) and the total stearic acid is precipitated as barium stearate by the addition of saturated aqueous barium hydroxide (400 ml). The salt is isolated by filtration, washed successively with water and ether, and dissolved in 15% hydrochloric acid (100 ml). The solution is extracted with ether (3 × 100 ml), dried with sodium sulfate, and evaporated. The residual product is purified by bulb-to-bulb distillation at ~0.01 torr; yield: 6.56 g (77%); m.p. 68–69° (Ref. [9], m.p. 69.4°).

(E)-4-Heptenoic Acid (**2p**); *Typical Procedure:* A mixture of (*E*)-4-heptenol (**1p**; 3.42 g, 30 mmol) and 1 molar aqueous sodium hydroxide (280 ml) is electrolyzed for 4 h at 25° using a current of 4 A (16 mA/cm^2) and a cell voltage of 2.0 V. Work-up consists of acidification with 12 normal hydrochloric acid (10 ml) and ether extraction (3 × 100 ml). Pure **2p** is obtained by bulb-to-bulb distillation at 116°/15 torr; yield: 3.14 g (82%).

$C_7H_{12}O_2$	calc.	C 65.60	H 9.44
(128.2)	found	65.76	9.46

M.S. (70 eV): m/e = 128 (M$^+$, 4%), 110 (37), 69 (62), 68 (100), 60 (38), 41 (82).

I.R. (film): ν_{max} = 3500–2500 (OH); 1705 (C=O); 965 cm^{-1} (CH=CH$_{trans}$).

^{1}H-N.M.R. (CCl$_4$): δ = 0.96 (t, 3H, CH$_3$); 1.8–2.2 (m, 2H, —CH$_2$—C=); 2.35 (m, 4H, =C—C$\underline{H}_2$—C$\underline{H}_2$—COOH); 5.3–5.6 (m, 2H, CH=CH); 11.5 ppm (s, 1H, COOH, exchangeable with D$_2$O).

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