

Electrolytic Oxidation of Isoborneol to Camphor

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The preparation of camphor by the anodic oxidation of isoborneol in NaCl and CaBr₂ electrolytes at different current densities using different diaphragms is described.

Isoborneol can be oxidized directly to camphor by chemical and electrolytic methods¹⁻⁴. Considerable literature on the former method is available whereas the literature on the latter is scanty.

This communication reports the anodic oxidation of isoborneol to camphor, since no details are available regarding either the type of cell used (electrodes, diaphragms, etc.) or the experimental conditions.

The electrolytic cell consists of a beaker in which a platinum cathode, a thermometer and a diaphragm are suspended. The diaphragm serves as a partition between the anode and the cathode and forms the anode compartment of the cell. Its upper open end is fitted with a rubber stopper carrying a lead dioxide anode, a stirrer (used only in the case of aqueous electrolytes) and a glass tube for the addition of electrolyte.

Carbon rods from Leclanche cell were used as electrodes, and unglazed porcelain diaphragm commonly employed in Leclanche cells, cellophane paper and sintered glass disc of porosity No. 3 were used as diaphragms. The pore size of the sintered disc was less in case of alkaline electrolytes.

The anode chamber was a glass tube with a sintered glass base of porosity No.3. This was placed in a beaker containing 5% aqueous NaCl for about 1 hr and then filled with the same solution. Isoborneol (1 g) was added to the anolyte and a current of 0.8A was passed for 6 hr using a carbon anode; a mechanical stirrer was used to emulsify so that the contact with the anode is improved. The current was kept constant by varying the voltage. At the end of the run, the reaction mixture was extracted thrice with ether, dried over Na₂SO₄ and ether evaporated. The presence of camphor was detected by comparative TLC on silica gel using CHCl₃ as the developing solvent and 0.4% dinitrophenylhydrazine in 2NHCl as the detecting agent. It was purified by regeneration through its semicarbazone. The yield was 0.215 g.

The experiment was repeated with carbon electrodes and cellophane paper as a diaphragm. The anolyte consisted of 1 g isoborneol in 1% NaCl (NaCl in 50% aq. CH₃OH; 100 ml) and the catholyte, 5% aq. NaCl, was added till the levels of the anolyte and the catholyte were the same in the cell. A current of 0.2A was passed

Table 1—Effect of Varying Current on the Yield of Camphor

Anolyte and catholyte: 7.5% aq. NaCl

Anode: carbon electrode, total immersed area: 42 cm²

Time: 2 hr

Current density A/cm ² × 10 ³	Amount of isoborneol g	Initial voltage V	Product g
24	4	18	0.585
20	4	15	0.554
12	4	11	3.41
6	4	75	1.82
3	4	5	—

for 6 hr. The reaction mixture (anolyte) was processed as before. It gave a product having m.p. 177°C, the m.p. of camphor. The yield was 0.4 g. It was purified by sublimation. It gave 2:4 dinitrophenylhydrazone, m.p. 177°C, semicarbazone, m.p. 237°C, and oxime, m.p. 118°C. Its infrared spectrum was superimposable with the spectrum of camphor.

A few experiments were carried out by varying only the quantity of electricity flowing through the solution. The variations in yield are shown in Table 1.

A few more experiments were conducted with carbon electrodes and CaBr₂ as the electrolyte (2.5%) at very low current densities (between 0.04 and 0.06 A/cm²) using an unglazed porcelain diaphragm. It was observed that the time required for the oxidation was much less than when NaCl was used as the electrolyte. The yields are also good. For example, in one such experiment when the oxidation was carried out with 2.5% CaBr₂ at a current density of 0.04 A/cm² using carbon as anode and cellophane as diaphragm the yield was almost 50% in 2 hr. The reaction was complete as shown by the absence of a spot, on TLC plate, corresponding to isoborneol.

Cellophane is a better diaphragm than sintered glass disc and unglazed porcelain pot of Leclanche cell, because cellophane offers little resistance to the passage of current and, unlike porous porcelain, is highly resistant to the passage of organic depolarizers. Besides, the porous porcelain membrane has a tendency to clog with a resultant increase in electrical resistance.

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