

Oxidation with Nitric Acid of Aliphatic Alcohols and Diols to Carboxylic Acids

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Received October 30, 2006

DOI: 10.1134/S1070428007050235

Aliphatic hydroxy compounds are oxidized to carbonyl derivatives by various oxidants, like potassium permanganate, chromium compounds, silver carbonate, ruthenium(VIII) oxide, nickel peroxide, potassium persulfate, etc. [1–3]. The oxidation of these compounds with nitric acid is performed far less often, although this oxidant is of great practical interest because of its low price and availability.

It was shown that the oxidation of primary alcohols with nitric acid gave rise as a rule to carboxylic acids with the same number of carbon atoms, and the oxidation of secondary alcohols occurred with a rupture of a carbon–carbon bond [4–11]. Thus the following acids were obtained at oxidation with nitric acids: from trimethylenechlorohydrin, chloropropionic [4], from glycerol, glyceric [5], from ethylene glycol, oxalic [6–9], and from triethylene glycol, glycolic [10] acids. The difficulties of this process consist in the choice of the reaction conditions and mainly in the separation of reaction products that even has been claimed in a patent [11].

We investigated the oxidation of some primary monohydric and dihydric alcohols containing a fairly long alkyl chain (from pentanol to undecanol), and also of ethylene glycol and 1,6-hexanediol.

The said alcohols suffered oxidation when treated with 30% and more concentrated HNO_3 . In oxidation of monohydric primary alcohols at 25–30°C the concentration of 70–85% is optimal. The reaction occurred with a high rate, with evolution of heat and nitrogen oxides, but is easily controlled by alcohol dosage and cooling the reaction mixture. Nitric acid of 75% and higher concentration contains a nitronium cation [12], therefore it is presumable that the primary product of the reaction

of HNO_3 with alcohols would be a nitric acid ester [13], and the formation of the final product, carboxylic acid, would depend on the chemical stability of the nitrate.

Primary aliphatic alcohols with a normal backbone of any length (pentyl, hexyl, octyl, decyl, and undecyl) are readily oxidized with nitric acid into the corresponding carboxylic acids in 75–90% yield, and this procedure can serve a preparative method for these acids.

The isoamyl alcohol contains a relatively labile hydrogen at the tertiary carbon atom; however under the chosen conditions the oxidation with the nitric acid does not affect the C–H bond, and the main product obtained is isovaleric acid.

The oxidation of dihydric primary alcohols depends on their structure as we have demonstrated by an example of 1,6-hexanediol and ethylene glycol. With two hydroxymethyl groups far removed from each other the 1,6-hexanediol behaved like monohydric alcohols and at treatment with the 75–85% nitric acid at 25–30°C easily underwent oxidation giving the adipic acid. The reaction occurred similarly to that with the monohydric alcohols with strong heat evolution and nitrogen oxides liberation, but the precipitation of adipic acid began immediately in the course of diol addition to HNO_3 .

The ethylene glycol oxidation also involved both hydroxy groups giving the oxalic acid, but it possessed certain specific features. For instance, on mixing the components the temperature first insignificantly increased, and after a short interval it rose to 60–65°C simultaneously with vigorous liberation of nitrogen oxides. The reaction mixture even required additional heating for the completion of the reaction. The relative stability of the ethylene glycol against the oxidation with the nitric acid may be

due to the stabilizing effect of the nitrate groups formed by esterification of the glycol.

Oxidation of alcohols. General procedure. To 80% nitric acid [63 g (1.0 mol) calculated on 100% HNO₃] at 25–30°C was added while stirring 0.2 mol of an appropriate alcohol. The reaction occurred with evolution of heat and nitrogen oxides that caused the brown color of the reaction mixture. After the end of heat evolution the reaction mixture was maintained for 3–4 h at 30°C till decoloration, then it was poured into 50 ml of cold water, extracted with chloroform (3×50 ml), the extract was dried with Na₂SO₄, the chloroform was distilled off, and the carboxylic acid obtained was purified by distillation.

Valeric acid was obtained from pentanol. Yield 90%, bp 186–187°C, n_D^{20} 1.4076 (bp 187°C, n_D^{20} 1.4086 [14]).

Caproic acid was obtained from hexanol. Yield 87%, bp 202°C, n_D^{20} 1.4136 (bp 202°C, $n_D^{19.6}$ 1.4145 [14]).

Caprylic acid was obtained from octanol. Yield 82%, bp 139–140°C (22 mm Hg), n_D^{20} 1.4275 (bp 237.5°C, n_D^{21} 1.4268 [14]).

Capric acid was obtained from decanol. Yield 80%, bp 136–138°C (8 mm Hg), mp 30°C (mp 31.5°C, bp 268°C [14]).

Undecanoic acid was obtained from undecanol. Yield 86%, bp 225–227°C (160 mm Hg), mp 29–30°C {mp 29–30°C, bp 228°C (160 mm Hg) [14]}.

Isovaleric acid was obtained from 3-methyl-1-butanol (isoamyl alcohol). Yield 20.5 g (81%), bp 175–176°C, n_D^{20} 1.4038. (bp 176°C, n_D^{20} 1.4043 [14]). IR spectrum, ν , cm⁻¹: 1720, 2720–3100 (COOH). ¹H NMR spectrum, δ , ppm: 0.9 t (6H, 2CH₃), 1.1 d (2H, CH₃), 1.6 m (1H, CH), 11.0 br.s (1H, COOH).

Adipic acid. To 80% nitric acid [63 g (1.0 mol) calculated on 100% HNO₃] at 25–30°C was added by small portions 23.6 g (0.2 mol) of 1,6-hexanediol. The separation of adipic acid started already during addition of the diol. After the end of diol addition the reaction mixture was maintained for 3–4 h till decoloration. Then the adipic acid was filtered off and dried. Yield 13 g (45%), mp 152°C (from water) (mp 151–153°C [14]).

Oxalic acid. *a.* To 80% nitric acid [63 g (1.0 mol) calculated on 100% HNO₃] at 25–30°C was added 12.5 g (0.2 mol) of ethylene glycol. After mixing the reagents the reaction mixture self-heated with vigorous nitrogen oxides liberation. When the mixture heated to 60–65°C it was cooled with water to 20°C, then gradually heated to 85–90°C and maintained at this temperature

for 4–5 h. The moderate nitric oxides evolution was controlled by the rate of heating. On cooling the mixture crystals of oxalic acid precipitated, were filtered off, and dried in air. Yield 17 g (69%). On recrystallization from water and drying in air oxalic acid dihydrate was obtained, mp 101°C (mp 101.5°C [14]).

b. On mixing the components the reaction mixture was maintained at 20°C for 7–10 days; therewith the crystals of oxalic acid started to precipitate in 2–3 days. Yield 80–85%.

In this study commercial primary alcohols were used and the 97% nitric acid of technical grade that was diluted with water to the required concentration. IR spectra were recorded on a spectrophotometer UR-20. ¹H NMR spectra were registered from solutions in acetone-*d*₆ on a spectrometer Tesla-497 at operating frequency 100 MHz at room temperature, internal reference HMDS.

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