

Oxidation of Ethers to Carboxylic Acids with Nitric Acid

N. V. Svetlakov, V. G. Nikitin, and E. A. Nikolaeva

Kazan State Technological University, Kazan, 420015 Russia

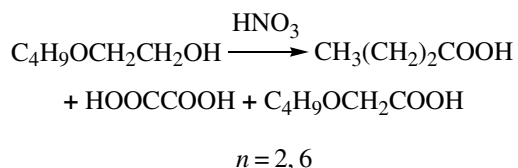
Received October 30, 2006

DOI: 10.1134/S1070428007050223

The C–O bond of the COC fragment in aliphatic ethers can be cleaved by nitric acid or nitrating mixtures to form alkyl nitrate with the same number of carbons in the alkyl group [1]. Depending on the presence in the carbon chain of the other functional groups the site of the reaction with the nitric acid may change. For instance, in reaction of a dioctyl ether with HNO₃ or its mixtures with other acids at 10°C the ether fragment is cleaved to give octyl nitrate [1], whereas the reaction of HNO₃ with diethylene glycol at 15–20°C resulted only in esterification of the terminal hydroxy groups leaving intact the ether moiety [2].

The nitric acid esters are relatively unstable chemical compounds, and we have presumed that they should convert in the nitric acid environment into carboxylic acids. The goal of this study was development of nitric acid reaction with ethers providing carboxylic acids.

We investigated the oxidation with 70–80% HNO₃ of dibutyl and dioctyl ethers, and also of 2-butoxyethanol. The ethers were subjected to oxidation at 30–40°C, the reaction occurred with evolution of heat and nitrogen oxides that caused the dark color of the reaction mixture. The completion of the reaction was judged by the end of heat evolution and by decoloration of the reaction mixture. The reaction products were butyric and caprylic acids respectively.



Our previous results [1] permit a conclusion that the primary product of the ether reaction with nitric acid is

an alkyl nitrate that is further oxidized into a carboxylic acid.

From products obtained in the reaction of 2-butoxyethanol with 80% HNO₃ at 30–40°C we isolated butyric, oxalic, and butoxyacetic acids.

Evidently here concurrent reactions occurred: hydroxymethyl group oxidation and ether bond cleavage leading to the formation of oxalic and butyric acids. The retention of the C–O–C bonds in the butoxyacetic acid resulted apparently from the decreased nucleophilicity of the oxygen atom caused by the nitrate group. This assumption is supported by the formation of diglycolic acid in oxidation of diethylene glycol by the nitric acid [3].

In oxidation of the 2-butoxyethanol under more severe conditions (70–80°C) the products lacked the butoxyacetic acid for it decomposed into oxalic and butyric acids.

Dialkyl ethers oxidation. General procedure. To 80% nitric acid [47 g (0.75 mol) calculated on the 100% HNO₃] was added at 35–40°C 0.1 mol of an appropriate ether. A self-heating of the reaction mixture was observed together with vigorous evolution of nitrogen oxides. The reaction temperature was maintained by cooling with an ice water bath. After 15–20 min from the moment of reagents mixing the evolution of heat and nitrogen oxides stopped. The reaction mixture was heated to 50°C for 2 h, cooled to 20°C, poured into 50 ml of water, and the products were extracted into chloroform (4×50 ml). The extract was dried, and the acid obtained was purified by distillation.

Butyric acid was obtained from dibutyl ether. Yield 11.6 g (66%), bp 83–84°C (39 mm Hg), n_D^{20} 1.3975 (bp 163°C, n_D^{20} 1.3979 [4]).

Caprylic acid was obtained from dioctyl ether. Yield 64%, bp 108°C (7 mm Hg), n_D^{20} 1.4290 (bp 237°C, n_D^{20} 1.4268 [4]).

2-Butoxyethanol oxidation. By oxidation with 80% HNO₃ at 30–40°C (molar ratio HNO₃:2-butoxyethanol 5:1) of 23 g (0.2 mol) of 2-butoxyethanol we obtained 5.7 g (32%) of butyric acid [bp 83–84°C (39 mm Hg), n_D^{20} 1.4136], 10 g (55%) of oxalic acid [mp 101°C (dihydrate)], and 5.5 g (10%) of butoxyacetic acid [bp 99–100°C (7 mm Hg), n_D^{20} 1.4245]. The oxalic acid precipitated and was filtered off, butyric and butoxyacetic acids were isolated by distillation.

The ethers used in the experiments were of “pure” grade, the concentrated nitric acid was of technical grade. 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.

REFERENCES

1. Svetlakov, N.V., Nikitin, V.G., and Ruziev, F.F., *Zh. Org. Khim.*, 2002, vol. 38, p. 312.
2. Orlova, E.Yu., *Khimii i tekhnologiiya brizantnykh vzryvchatykh veshchestv* (Chemistry and Technology of High Explosives), Moscow: Oborongiz, 1960, p. 301.
3. Svetlakov, N.V., Nikitin, V.G., and Orekhova, A.O., *Zh. Org. Khim.*, 2002, vol. 38, p. 789.
4. *Spravochnik khimika* (Chemist's Handbook), Moscow: Khimiya, 1963, vol. 2, p. 768.