

Octane Oxidation into Carboxylic Acids

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

Kazan State Technological University, Kazan, 420015 Russia

Received November 9, 2004

Saturated aliphatic hydrocarbons because of low reactivity enter into chemical reactions at elevated temperature and as a rule by radical mechanism [1]. A wide practical application has found the oxidation of solid and liquid paraffins into aliphatic alcohols and carboxylic acids by air oxygen in the presence of catalysts at the temperature over 100°C [2].

We showed formerly [3] that saturated aliphatic hydrocarbons at 18–20°C reacted with a mixture of nitric acid and acetic anhydride furnishing an isomer mixture of secondary alcohols nitrates. The secondary alcohols and their derivatives are also known to suffer oxidation with the nitric acid to monocarboxylic acids with the cleavage of the hydrocarbon chain [4]. Therefore the carboxylic acids may be obtained from paraffins via alkyl nitrates by further decomposition of the latter into acids.

The octane oxidation to monocarboxylic acids was performed in two stages: First octane was treated at 18–20°C with a mixture of nitric acid and acetic anhydride aiming at preparation of alkyl nitrates, and then the temperature was raised to 30°C; therewith the alkyl nitrates decomposed affording a mixture of monocarboxylic acids. The acids were extracted with chloroform after diluting the reaction mixture with water. We succeeded to isolate valeric, caproic, and heptanoic acids. The acids of smaller molecular weight cannot be isolated by this procedure due to high solubility in water.

Taking into account the high electrophilicity of the reaction medium and low oxidation temperature the reaction presumably occurs by ionic mechanism. We used octane of “pure” grade, nitric acid and acetic anhydride of “technical” grade.

To a mixture of 232 g (3.68 mol) of 98% HNO₃ and 94 g (0.92 mol) of acetic anhydride at 20°C while vigorous stirring was added dropwise 25 g (0.22 mol) of octane, and at 18–20°C the reaction mixture was kept for

1.5–2 h till the end of nitrogen oxides evolution and decoloration of the reaction mixture. Then the reaction mixture was warmed to 30°C for 2 h and left standing at 20°C for 12 h. Afterwards the reaction mixture was poured into cold water (400 ml), and the reaction products were extracted into chloroform (3×100 ml). The extract was washed with water and dried on Na₂SO₄. Chloroform was distilled off, and the obtained acids mixture (20–22 g) was separated by vacuum distillation.

Valeric acid, bp 58–59°C (9 mm Hg), n_D^{20} 1.3989 (publ.: bp 187°C, n_D^{20} 1.409 [5]). Acid number: found 377, calculated 382. IR spectrum, ν , cm⁻¹: 1720, 2600–3100 (COOH). ¹H NMR spectrum, δ , ppm: 0.25 t (3H, CH₃), 0.5 m (4H, 2CH₂), 0.9 t (2H, CH₂COO⁻), 5.2 br.s (1H, COOH).

Caproic acid, bp 88–89°C (9 mm Hg), n_D^{20} 1.4180 (publ.: bp 202°C, n_D^{20} 1.4145 [5]). Acid number: found 338, calculated 336. IR spectrum, ν , cm⁻¹: 1720, 2750–3200 (COOH). ¹H NMR spectrum, δ , ppm: 0.92 t (3H, CH₃), 1.23 m (6H, 3CH₂), 2.01 t (2H, CH₂COO⁻), 10.05 br.s (1H, COOH).

Heptanoic acid, bp 103°C (9 mm Hg), n_D^{20} 1.4233 (publ.: n_D^{20} 1.4216 [5]). Acid number: found 299, calculated 300. IR spectrum, ν , cm⁻¹: 1715, 2720–3100 (COOH). ¹H NMR spectrum, δ , ppm: 0.96 t (3H, CH₃), 3.2 t (2H, CH₂COO⁻), 4.4 m (8H, 4CH₂), 13.8 s (1H, COOH).

Weight ratio of valeric, caproic, and heptanoic acids was 1:1:3.

IR spectra of carboxylic acids were recorded on a spectrophotometer UR-20. ¹H NMR spectra were registered on spectrometer Tesla-497 at operating frequency 100 MHz at room temperature from solutions in acetone-*d*₆, internal reference HMDS.

REFERENCES

1. *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 1.
2. Tsyskovskii, V.K., *Sintez zhirnykh kislot i spirtov okisleniem zhidkikh parafinov* (Synthesis of Fatty Acids and Alcohols by Oxidation of Paraffin Liquids), Leningrad: GNTIKhL, 1960, p. 14.
3. Svetlakov, N.V., *Zh. Org. Khim.*, 1998, vol. 34, p. 1137.
4. Shabarov, Yu.S., *Organicheskaya khimiya: Uchebnik dlya vuzov* (Organic Chemistry: Course of Chemistry for University), Moscow: Khimiya, 2002, vol. 192, p. 260.
5. *Spravochnik khimika* (Handbook of Chemist), Moscow: Khimiya, 1964, vol. 2, pp. 566, 712, 1116.