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BRIEF COMMUNICATIONS

Cyclohexanol Nitration by a Mixture of Ammonium Nitrate and Sulfuric Acid in a Two-Phase System

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Abstract—Cyclohexanol nitration by a mixture of ammonium nitrate and sulfuric acid in the presence of an organic solvent was studied.

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Cyclohexyl nitrate (CHN) is an effective addition agent raising a cetane number of diesel fuel [1]. One of promising methods of CHN synthesis is the cyclohexanol nitration by a mixture of sulfuric and nitric acids, however it requires lower temperatures (–20…–30°C) owing to the tendency of cyclohexanol and CHN to be oxidized by nitric acid [2, 3].

It is known that the application of nitrating mixtures with increased water contents or of mixtures based on nitric acid salts allows the temperature of cyclohexanol nitration to be increased up to 5–10°C [4, 5]. However, as a result of side processes a hazard of an uncontrollable decomposition of the waste acid mixture accompanied by heat and gas release increases. The use of an inert organic solvent in the cyclohexanol nitration by a sulfuric-nitric mixture makes it possible to increase the CHN yield and the admissible temperature of the process up to 10–15°C, but in this case the probability of the decomposition of the acid layer remains, which demands its fast separation and neutralization [6, 7]. The uncontrollable heat effect gives rise to a hazard of exceeding the process critical temperature and thus can result in contingency situations connected with equipment decompression, ejection of a reaction mass, and complete product loss.

It was found that the application of an ammonium nitrate and sulfuric acid mixture in combination with addition of an inert solvent makes it possible to increase the yield of a reaction product and to raise considerably stability of the waste acid mixture. Conditions and results of the experiments are given in the table; the nitrating mixture composition is specified without taking into account formed ammonium bisulfate.

For comparison we used solutions of ammonium nitrate (experiments nos. 1–6) and nitric acid (experiments nos. 7, 8) in sulfuric acid, taking methylene chloride as an inert solvent. The highest yield was reached for the nitrating mixture containing 3.5% of water at the nitration temperature of 10–11°C (experiment no. 4). Decrease in sulfuric acid concentration (experiment no. 5) or in ammonium nitrate excess (experiment no. 6), and also the absence of the organic solvent cause uncontrollable heat release while an alcohol dosing, which hinders the reaction completion. The composition of the nitrating mixture obtained when nitric acid was used (experiments nos. 7, 8) was selected as optimal on the basis of a series of previous experiments.

Stability of the waste acid mixture after separation of layers was estimated by varying its temperature during holding in equal conditionals without effective cooling. The results obtained are shown in the figure.

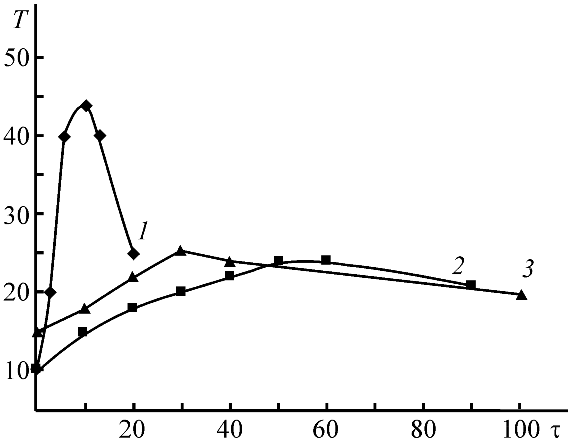
As follows from the figure, when ammonium nitrate is used instead of nitric acid, exhausted nitro mixture is heated up much slower and only by a few degrees higher than the temperature of ambient air (19–20°C). The organic layer containing the main part of the product after acid separation appears sufficiently stable without backwashing.

Nitrating mixtures based on ammonium nitrate are characterized by the absence of nitrous acid initiating oxidative processes. Furthermore, the presence of ammonium salts decreases CHN solubility in the waste acid, which on the whole is responsible for the increase in the process stability. Thus, owing to the reached decrease in the rate of nitromass decomposition, the necessity of the fast CHN separation after the reaction and of the acid layer dilution with water is excluded. According to GLC data, the resulting CHN samples contain no more than 1.4% of cyclohexanone.

EXPERIMENTAL

The GLC analysis was carried out on a Khromos GKh-1000.1 instrument; a steel column 1 m × 3 mm; temperature of an evaporator and PID 210, of the column 80°C; the stationary immobile phase 5% SE-30; the carrying agent Chromaton-N-AW; the gas-carrier helium; the volume flow rate 30 ml min^{-1}.

Nitration of cyclohexanol with application of ammonium nitrate (experiment no. 4). NH_4NO_3, 5.7 g (0.071 mol), was dissolved in 20 g of 97% H_2SO_4 at 10–15°C and held within 1 h. At first 15 ml of CH_2Cl_2 was added to the resulting mixture and then 4.7 g (0.047 mol) of cyclohexanol was dosed with intensive stirring, maintaining temperature at 10–11°C. After dosing termination the reaction mass was stirred for 10 min more and then layers were separated. An organic layer was sequentially washed out by 50 ml of water, 50 ml of 4% Na_2CO_3 solution, again by water, and dried by anhydrous Na_2SO_4. A solvent was removed on a rotor evaporator, and 6.5 g (95%) of cyclohexyl nitrate was obtained. The acid layer was placed back in a reactor and held with mixing without additional cooling.



Character of heat release during holding exhausted acid mixture. (*T*) temperature of mixture (°C), (τ) time after separation of acid layer (min). After nitration: (*1*) using HNO_3; (*2*), (*3*) using NH_4NO_3 at 10–11 and 14–15°C, respectively.

Results of cyclohexanol nitration by sulfuric-nitric acid mixtures

Experiment no.	Amount of the initial components,[a] g			Calculated composition of nitrating mixture, %			Molar HNO_3 excess	Temperature of nitration, °C	CHN yield, %
	HNO_3 (97%)	NH_4NO_3	H_2SO_4 (94%)	HNO_3	H_2SO_4	H_2O			
1	–	5.7	20.0	25.7	67.5	6.8	1.5	4…5	87
2	–	5.7	20.0	25.7	67.5	6.8	1.5	10…11	85
3	–	5.7	20.0	25.7	67.5	6.8	1.5	14…15	82
4	–	5.7	20.0[b]	25.6	70.9	3.5	1.5	10…11	95
5	–	5.7	15.0	35.9	56.9	7.2	1.5	10…11	–
6	–	4.5	15.8	25.5	67.2	7.3	1.2	10…11	–
7	4.5	–	12.0	26.4	68.4	5.2	1.5	10…11	88
8	4.5	–	12.0	26.4	68.4	5.2	1.5	14…15	74

[a] Amount of methylene chloride in all experiments was 15 ml.

[b] Concentration of sulfuric acid was 97%.

Nitration of cyclohexanol with nitric acid application (experiment no. 7). To a mixture of 12.0 g of 94% H_2SO_4 and 4.5 g (0.069 mol) of 97% HNO_3 10 ml of CH_2Cl_2 was added, and 4.7 g (0.047 mol) of cyclohexanol was dosed with stirring, maintaining temperature of 10–11°C. After dosage termination the reaction mass was held for 5 min and treated as described above to obtain 6.0 g (88%) of cyclohexyl nitrate.

CONCLUSION

Mixtures of ammonium nitrate and sulfuric acid containing 3.5% of water with addition of methylene chloride are most suitable for a safety cyclohexanol nitration. Necessary molar excess of nitric acid is 1.5 and the optimal process temperature is 10–11°C.

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