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Abstract

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On the Interaction of Cyclohexene with Concentrated Nitric Acid

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The nitration of cyclohexene and the mechanism of this reaction have been investigated in a number of works ($^{1-6, 8-10}$). In these works, nitrogen oxides or dilute nitric acid were used as nitrating agents. The reaction was studied in the liquid phase.

In the present work, we investigated the interaction of cyclohexene with highly concentrated nitric acid (from 98.5 to 99.7% in different experiments) in the vapor phase, at a ratio between acid and hydrocarbon calculated for complete oxidation (combustion) of the hydrocarbon (5.2 : 1 by weight). The reaction was carried out at atmospheric pressure in a quartz tube 20 mm in diameter at 100° and a contact time of 6.5 sec. Separate experiments were conducted at a contact time of 1.63 sec. It was established that, as a result of the reaction, a complex mixture of products is formed, containing, in various combinations, nitro, nitroso, nitrate, hydroxyl, carbonyl, and carboxyl groups. It is not excluded that, in accordance with the data of Baldock, Levy, and Scaife (^{5}), a compound containing a nitrite group is also formed—cyclohexene nitronitrite. The latter may hydrolyze during processing, forming nitrocyclohexanol. The following reaction products were isolated and identified: cyclohexene pseudonitrosite, nitrocyclohexanone, 1-nitrocyclohexene, ketocyclohexylnitrate, nitrocyclohexylnitrate, dinitrocyclohexane, 1,2-cyclohexanedione, a compound with the empirical formula $C_6H_{10}O_2$, 2-nitrocyclohexanol, mononitrate of 1,2-cyclohexanediol, adipic acid, oxalic acid, and succinic acid.

It was established that in those cases where cis-trans isomerism is possible for the isolated compounds, as a rule a mixture of isomers is formed with predominance of the trans form.

Thus, the investigation showed that, under the conditions of the experiments carried out, the interaction of cyclohexene with concentrated nitric acid is a complex reaction in which oxidation processes play a substantial role.

The investigation carried out is of particular interest for understanding the process of spontaneous ignition of cyclohexene with concentrated nitric acid. The accumulation of nitrates (and possibly nitrites) during the preflame period apparently plays an essential role in the indicated process of spontaneous ignition. This supposition is confirmed by the results of comparing the spontaneous-ignition temperature of cyclohexene with nitric acid and the isolated reaction products, as well as by the shortening of the so-called "thermal induction period of spontaneous ignition" of cyclohexene with nitric acid in the case of preliminary addition to the hydrocarbon of the nitrates formed in this reaction*. A more substantiated judgment about the chemistry of the interaction and spontaneous ignition of cyclohexene with nitric acid can be done after completion of work on investigating the kinetics of accumulation, in the preflame period, of intermediate—primarily unstable—products of this reaction.

Experimental Part

The investigation was carried out in a specially constructed apparatus. The liquid components of the reaction—nitric acid (distilled, with a nitrogen oxide content of 0.28-0.3%) and cyclohexene (b.p. 83°, d_4^{20}0.8107, n_D^{20}1.4470)—were fed under pressure from vessels through capillaries into evaporators. The required ratio between them was maintained by selecting the pressure drop across the capillaries. From the evaporators, the vapors of nitric acid and cyclohexene passed through coils maintained at 100° into a mixer and then into a reaction tube, the length of which ensured the prescribed contact time. The reaction products were condensed in four traps connected in series and cooled with liquid nitrogen. The reaction mixture was treated with ice water; the dark-green oily product that settled to the bottom was separated from the aqueous layer, washed several times with cooled water, and dissolved in ether. If cyclohexene pseudonitrosite was formed in the reaction, crystals precipitated from the ethereal solution. After separation of the crystals, the ethereal solution was neutralized with a 10% sodium bicarbonate solution, then washed with water and dried with magnesium sulfate. The ether was distilled off, and the dry oil was distilled in vacuo into narrow fractions. A small amount of solution was taken from the aqueous layer for isolation of dibasic acids. The remaining portion of the aqueous layer was neutralized, under cooling, with dry sodium bicarbonate and extracted repeatedly with ether. The extracted products were distilled into narrow fractions in vacuo. After separation of the neutral products, the aqueous layer was acidified for extraction of the acids.

Cyclohexene pseudonitrosite precipitates from the ethereal solution of the oily reaction product (see above). It was isolated in experiments with a contact time of 1.63 sec (48 g from 830 g of initial cyclohexene). After three recrystallizations from ethyl acetate—crystals with m.p. 145-145.5°. A mixed sample with synthesized cyclohexene pseudonitrosite melts at 146°.

Nitrocyclohexanone* was isolated from the fraction of the oily layer with b.p. 54-60° at < 1 mm (after separation of crystals that had precipitated earlier as a flocculent precipitate (0.09 g), which spread in air into a viscous dark-brown

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* The results of these investigations will be published.

mass). The precipitate fell out upon cooling the ethereal solution of the fraction to −20°. It was identified by preparation of the phenylhydrazone, which after three recrystallizations from alcohol melts at 125.5–128.5°,

$C_{12}H_{15}N_3O_2$. Found %: C 61.86; 61.80; H 6.64; 6.66; N 18.72; 18.77
Calculated %: C 61.8; H 6.43; N 18.02

and also by the IR spectrum of the phenylhydrazone when compared with literature data (7).

1-Nitrocyclohexene was identified in the fraction of the oily layer with b.p. 60–64° at < 1 mm (9 g): $n_D^{20} 1.5055$; $d_4^{20} 1.1354$; $MR_D 33.2$ (calculated 32.86); it decolorizes bromine in a carbon tetrachloride solution.

$C_6H_9O_2N$. Found %: C 56.59; 56.63; H 7.04; 7.08; N 11.0; 10.88
Calculated %: C 56.7; H 7.1; N 11.02

The presence of 1-nitrocyclohexene, according to IR spectral analysis, was also established in other fractions of the oily layer (11.62 g): a) in fractions with b.p. 74–76° and 80–82° at 1 mm (in predominant amount, along with ketocyclohexyl nitrate and nitrocyclohexanol); b) in fractions with b.p. 87–90°, 90–94°, and 95–96° at <1 mm (in a mixture with ketocyclohexyl nitrate, the amount of the latter increasing with increasing boiling point of the fraction).

Ketocyclohexyl nitrate was isolated in the form of crystals from the fraction of the oil layer with b.p. 97-99° at 1 mm (18.36 g) upon cooling it with dry ice. Recrystallized from petroleum ether. M.p. 31.5-32.2°.

$C_6H_9NO_4$. Found %: C 45.69; 45.79; H 5.68; 5.69; N 8.91; 8.86
Calculated %: C 45.28; H 5.66; N 8.88

The **2,4-dinitrophenylhydrazone of ketocyclohexyl nitrate** melts at 118–119°.

$C_{12}H_{13}O_7N_5$. Found %: C 43.12; 43.10; H 3.95; 4.19; N 21.99; 21.54
Calculated %: C 42.5; H 3.83; N 20.6

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* Here and below are given the results of investigation of the reaction at a contact time of 6.5 sec. In all, 3192 g of nitric acid and 614 g of cyclohexene were consumed.

According to infrared spectral analysis, ketocyclohexyl nitrate is also present in fractions boiling at a higher temperature (up to the fraction with b.p. 107-110° at 1 mm—22.6 g).

Nitrocyclohexyl nitrate—fraction of the oil layer with b.p. 123-125° at 1 mm (1.72 g), n_D^{20} 1.4932; d_4^{20} 1.3342; MR_D 41.39 (calculated 41.46); molecular weight 182 (calculated 190).

$C_6H_{10}N_2O_5$. Found %: C 37.77; 37.80; H 5.37; 5.14; N 14.68; 14.44
Calculated %: C 37.9; H 5.26; N 14.73

It was also identified by its infrared absorption spectrum by comparison with the spectrum of a synthesized product and with literature data (^{7}). Fractions with boiling point from 112 to 122° at 1 mm (18 g), according to infrared spectral analysis, contain significant amounts of nitrocyclohexyl nitrate, as well as a small amount of ketocyclohexyl nitrate.

Dinitrocyclohexane—fraction of the oil layer with b.p. 110-115° at <1 mm (2.53 g), n_D^{20} 1.4929; d_4^{20} 1.3260; MR_D 38.12 (calculated 38.45).

$C_6H_{10}N_2O_4$. Found %: C 40.94; 40.95; H 5.48; 5.41; N 15.9; 16.1
Calculated %: C 41.4; H 5.7; N 16.0

1,2-Cyclohexanedione was isolated when the reactions were carried out under conditions somewhat different from those described above. In particular, vapors of nitric acid and cyclohexene entered the mixer at 90°, and toward the end of the reaction the cyclohexene feed rate was increased. Fraction of the oil layer with b.p. 53-54° at <1 mm, n_D^{20} 1.5065; d_4^{20} 1.1305.

$C_6H_8O_2$. Found %: C 64.23; 64.28; H 7.11; 7.13
Calculated %: C 64.28; H 7.14

The **phenylhydrazone** of the obtained diketone, after recrystallization from alcohol, melts at 149.5-150.5°. A mixed sample with the phenylhydrazone of 1,2-cyclohexanedione of known structure melted at 150-151°.

$C_{18}H_{20}N_4$. Found %: C 74.10; 73.93; H 6.88; 6.74; N 18.31; 18.46
Calculated %: C 74.00; H 6.85; N 19.15

The **product with empirical formula** $C_6H_{10}O_2$ precipitates as white crystals (3.03 g) from the fraction of the aqueous layer with b.p. 50-90° and 46-48° at 1 mm when they are cooled to 0-+5°. After recrystallization from ethyl acetate it melts at 136-137°.

Found %: C 62.76; 62.65; H 9.04; 8.9

On treatment of product 1 N with an aqueous NaOH solution for 26 hours at room temperature, adipic acid was isolated (upon acidification). The structure of the indicated compound is currently being established.

2-Nitrocyclohexanol was isolated in the form of crystals from the aqueous-layer fraction with b.p. 88–90° at <1 mm (4.75 g) upon cooling it to 0–+5°; it was recrystallized from ligroin, m.p. 46–47.2°. The melting point of a mixed sample with synthetic 2-nitrocyclohexanol was 46.5–47.5°. The derivative with 3,5-dinitrobenzoyl chloride melted at 145–146°. No depression of the melting point of mixed samples with a derivative of synthesized 2-nitrocyclohexanol was observed.

Found, %:	N 12.32; 12.48
$C_{12}H_{13}N_3O_8$. Calculated, %:	N 12.39

According to IR spectral analysis, 2-nitrocyclohexanol is present in a mixture with mononitrate of 1,2-cyclohexanediol also in fractions with b.p. up to 97° at <1 mm (total 7.44 g).

Mononitrate of 1,2-cyclohexanediol was identified from the IR absorption spectrum in the aqueous-layer fractions with b.p. 88–90° and 91–94° at <1 mm by comparison with the spectrum of synthetic mononitrate of 1,2-cyclohexanediol and the data reported by Brown (7).

Adipic acid was isolated from the ether extract obtained upon extraction of the acidified aqueous layer. After three sublimations it melted at 150–150.8°. The m.p. of a mixed sample with pure adipic acid was 150–150.7°.

Oxalic acid was isolated from a mixture of dibasic acids obtained in the residue after evaporation of a sample of the aqueous layer (see above). The dry residue was dissolved in water. By addition of a saturated solution of calcium chloride, the acid was precipitated as the calcium salt. The precipitated salt was washed several times with hot water and decomposed with 30% HCl. By repeated extraction with ether, oxalic acid was extracted from the aqueous solution. After three sublimations the acid melted at 186°. The m.p. of a mixed sample with pure oxalic acid was 186–187°.

Found, %:	C 26.61; 26.73;	H 2.22; 2.23
$C_2H_4O_2$. Calculated, %:	C 26.67;	H 2.23

Succinic acid was detected qualitatively in the mixture of dibasic acids by the intense yellow-green fluorescence (formation of succinylfluorescein).

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Note: Figure translations are in progress. See original paper for figures.