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Ozone Reaction with 2,4-Dinitrotoluene in Acetic Acid Solution

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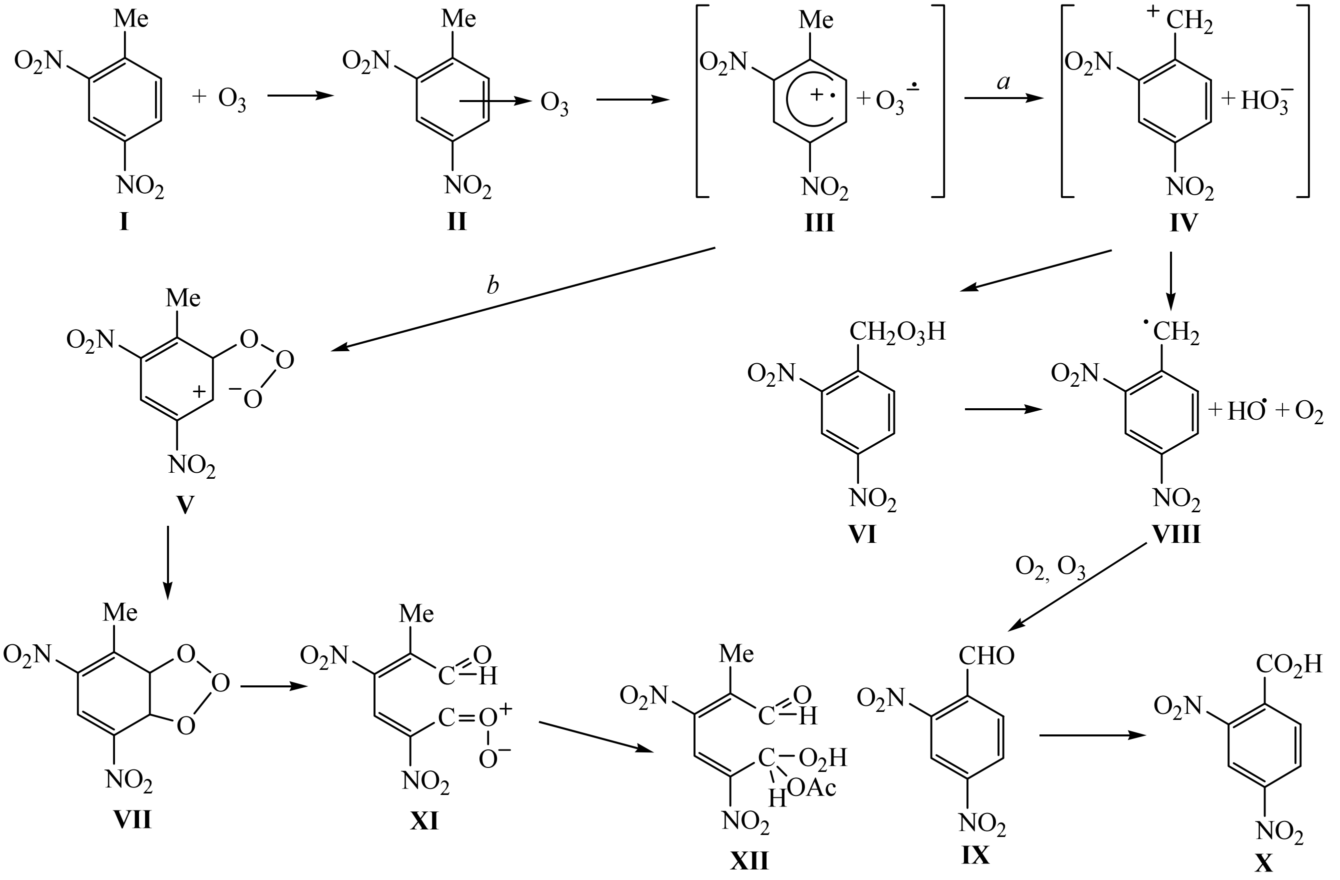
Abstract—2,4-Dinitrotoluene reacts with ozone along two concurrent pathways: at the aromatic ring yielding stable against ozonolysis hydroperoxide, and at the methyl group with retention of the aromatic structure. The relative amount of products undergoing oxidation at the aromatic ring and at the methyl group depends on the ozonation conditions, especially on the process temperature.

We showed previously by an example of ozone reaction with 4-nitrotoluene that introduction of electron-withdrawing substituents into the *para*-position of the toluene aromatic ring decreased the aromatic system destruction by ozone: The fraction of products from the ozone reaction at the methyl group grew from 16.0% in toluenea to 24.2% in 4-nitrotoluene [1, 2].

In extention of this study we investigated by an example of the ozone reaction with 2,4-dinitrotoluene the effect of the second nitro group attached to the *ortho*-



position on the reaction direction and reaction products composition.

At 323 K ozone reacts with dinitrotoluene (**I**) in the same way as with 4-nitrotoluene [2] along two competing pathways: at the methyl group (*a*) and at the aromatic ring (*b*) (see table and figure). The main products of the destructive oxidation of the aromatic ring are peroxide compounds **XII**, and the selective oxidation affords 2,4-dinitrobenzoic acid (**X**); the oxidation products accumulate concurrently. In the oxidation at the methyl group intermediately forms 2,4-dinitrobenzaldehyde (**IX**) that in case of exhaustive oxidation of **I** transforms into acid **III**. The ratio of products originating from the oxidation at the methyl group and at the aromatic ring is 1 : 1.3; meaning that under experimental conditions at 323 K the selective oxidation at the methyl group does not exceed 42%. Hence each successive introduction into the aromatic ring of toluene of an electron-withdrawing substituent like the nitro group results in growing selectivity of oxidation at the methyl group.

Taking into account the experimental and published data [3, 4] the ozone reaction with dinitrotoluene (**I**) may be represented in a scheme involving formation of a π-complex **II** in the course of the process. The key point in the scheme is the stage of an electron transfer resulting in formation of cation-radical from the aromatic substrate and of anion-radical from ozone **III** that further undergo transformations along two pathways affording either σ-complex **V** or ion pair **IV**. Ion pair **IV** at low temperature (233–200 K [5]) is converted into hydro-trioxide **VI** and further into radical products of the process **VIII.** At 323 K the hydrotrioxide **VI** is unstable, and the ion pair **IV** provides the radical reaction products bypassing the hydrotrioxide **VI** formation.

In keeping to the scheme in the ozone reaction with benzene [6] σ-complex **V** converts into molozonide **VII** with subsequent ring opening and formation of a bipolar ion **XI** that in the acetic acid is present in the form of hydroperoxide **XII**. The monomer structure of hydroperoxide **XII** was confirmed by the following facts: Firstly, the hydroperoxide in question reacted with potassium iodide in 3 h giving the molecular iodine in a quantity equivalent to one peroxy group; secondly, the stoichiometric factor of ozone in reaction at the aromatic ring was 1.24, i.e. was close to unity.

Oxidation of 2,4-dinitrotoluene (**I**) (2.5 h)[a]

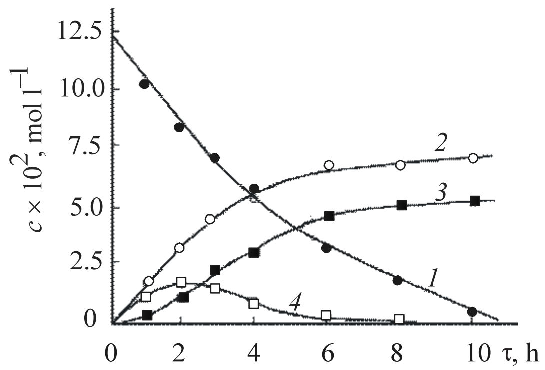
T, K	Conversion, %	*k*, $l\ mol^{-1}\ s^{-1}$	*v*, $l\ mol^{-1}\ s^{-1}$	Yield of oxidation products, %		
				XII	**IX**	**X**
303	18	0.0167	7.31×10^{-7}	61	6	28
323	44	0.1578	1.85×10^{-6}	53	10	29
343	59	0.3791	3.70×10^{-6}	51	9	35
373	75	0.8682	6.89×10^{-6}	48	6	40
373	100	0.8682	6.89×10^{-6}	50	0	47

[a] *k* is rate constant, *v* is rate of oxidation of compound **I**.

The relative amounts of oxidation products at the methyl group and the aromatic ring depend on the ozonation conditions, especially on the temperature (see Table). With the growing temperature the overall initial oxidation rate and the rate of acid **X** formation increase. At 323 K the pathway *b* dominates, the selectivity of oxidation at the methyl group does not exceed 42%. With growing temperature the fraction of products of oxidation at the methyl group increases and at 373 K attains 48%.

EXPERIMENTAL

Ozonation of compound **I** was performed in a reactor consisting of a glass column of capacity 0.03 l equipped with fine-pore fritted disc for dispersing the gas mixture. The reactor was charged with 0.015 l of glacial acetic acid and 0.125 mol l^{-1} of substrate **I**, the reactor was kept at controlled temperature, and the ozone-oxygen mixture was passed thereto at a rate $8.3 \times 10^{-3}\ l\ s^{-1}$. The amount of initial compound **I** and of the intermediate oxidation products in the reaction mixture was determined by GLC on a chromatograph LKhM-80 equipped with a flame-ionization detector and a column 2 m long packed with Chromaton N-AW with applied thereto stationary



2,4-Dinitrotoluene (**I**) oxidation with ozone in acetic acid. (*1*) 2,4-dinitrotoluene (**I**), (*2*) peroxides **XII**, *3* – 2,4-dinitrobenzoic acid (**X**), *4* – 2,4-dinitrobenzaldehyde (**IX**) {323 K, $V(O_2)$ 8.3 $l\ s^{-1}$, $[ArH]_0$ 0.125 mol l^{-1}, $[O_3]_0$ 9.5×10^{-4} mol l^{-1}}.

phase PNFS-6. The concentration of acid **X** formed was determined by alkaline titration.

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