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Effect of medium acidity on the efficiency of oxidation of 2,4,6-trinitrotoluene to 2,4,6-trinitrobenzoic acid

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An effect of boric acid additives on oxidation of 2,4,6-trinitrotoluene (TNT) to 2,4,6-trinitrobenzoic acid (TNBA) with chromic anhydride in concentrated (96—100%) H_2SO_4 has been studied. In the presence of tetrahydrosulfatoboric acid $HB(HSO_4)_4$ formed *in situ* (up to 5 mol.%) or added as a preliminary prepared solution (up to 1 mol. %), TNT is selectively oxidized to TNBA in the yields up to 95—99%. The mechanism including formation of TNT dication as a key step of its oxidation at the methyl group has been suggested.

Key words: 2,4,6-trinitrotoluene, tetrahydrosulfatoboric acid, 2,4,6-trinitrobenzoic acid, oxidation, chromic anhydride, cation-radicals, dications.

Oxidation of the methyl group of the substituted toluenes is one of important synthetic approaches to practically valuable products.[1] If the aromatic ring contains electron-donating substituents activating the molecule, the oxidation depth can be controlled through the choice of an approariate oxidant. Introduction of one or especially more electron-withdrawing substitutents in the aromatic ring deactivates the molecule to oxidation. In this case, the oxidation potential of a compound is considerably increased while the reaction selectivity decreases: under drastic conditions the oxidation of the methyl group is accompanied with the undesired exhaustive oxidation to carbon dioxide and water.

In the present study, oxidation of 2,4,6-trinitrotoluene (TNT) to 2,4,6-trinitrobenzoic acid (TNBA) is considered. This process is important both from practical and theoretical points of view. Based on 2,4,6-trinitrobenzoic acids, a variety of heterocyclic systems has been synthesized[2,3] being half-products in the synthesis of biologically active molecules, dyes, and aromatic condensation polymers. Decarboxylation of TNBA under mild conditions in turn smoothly affords practically valuable 1,3,5-trinitrobenzene.[4,5]

Oxidation of polynitrotoluenes requires high potentials of an oxidation system. Direct oxidation of polynitrotoluenes on an electrode (anode) found no practical application because of low efficiency.[6] In our previous studies, we have developed an electrochemical method for tervalent cobalt-mediated oxidation of polynitrotoluenes in concentrated nitric acid at temperatures of 35—40 °C.[7,8] In contrary to the electrochemical oxidation of TNT to TNBA, chemical oxidation of TNT to TNBA proceeds under rather drastic conditions. For example, a procedure to obtain TNBA through oxidation of TNT by nitric acid at 180—190 °C under pressure of 35—40 atm is known.[9]

Oxidation of TNT with sodium dichromate[10] or chromic anhydride[11] in concentrated sulfuric acid at 40—55 °C has long and widely been used as a laboratory method to obtain TNBA. Over many years one managed to improve this method,[12,13] in particular, by adding acetic acid to a reaction mixture.[13] However, no explanations of a change in the TNBA yield depending on the synthetic conditions were given in these studies.

From our point of view, the problems connected with rising the TNBA yield are due mainly to the fact that oxidation of TNT to TNBA proceeds effectively only at very high potentials of the redox system. Potential of a $Cr_2O_7^{2-}/Cr^{3+}$ system should increase with growth of the medium acidity. Therefore, it may be suggested that oxidation of TNT with chromic anhydride should be carried out not only in concentrated acid but probably in the presence of superacids. To confirm this proposal, we performed oxidation of TNT with chromic anhydride in concentrated sulfuric acid in the presence of boric acid.

Results and Discussion

As underlined above, for effective oxidation of TNT to TNBA high oxidation potential of the system E_{ox} is necessary. Approximate evaluation using the Nernst equation with account of the Hammett acidity function (H_o) shows that for the redox system $Cr_2O_7^{2-}/Cr^{3+}$ the value of E_{ox} grows from 2.3 to 2.7 V upon changing the sulfuric acid concentration from 75 to 95%.[14—16] We have found exper-

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imentally that on performing the oxidation of TNT in 75% sulfuric acid the yield of TNBA is 45%, while in 98% H_2SO_4 it rises up to 70%. Thus, to raise the yield of TNBA one should maximize E_{ox} of the redox system by raising the medium acidity.

Acidity of sulfuric acid can be significantly increased by adding boric acid. The H_0 value for the H_3BO_3 solutions in concentrated H_2SO_4 may reach −13.62,[17,18] while for 98% H_2SO_4 it is only −10.41.[15] To determine experimentally the effect of H_3BO_3 on the yield of TNBA, TNT was oxidized with chromic anhydride at various concentrations of H_2SO_4 and H_3BO_3. In all cases, chromic anhydride was used in a small excess (20 mol. %). Known procedures were applied to perform oxidation of TNT, isolation, and purification of TNBA.[10,19] Results are shown in Table 1. Yields of TNBA and picric acid (PA) were calculated based on the reacted TNT.

From the data presented in Table 1, it follows that an increase in the acidity of the medium due only to the rise in the concentration of H_2SO_4 results in the noticeable growth of the TNBA yield, namely, from 65 up to 81%, even *per se*. Addition of boric acid at any of the examined concentration of H_2SO_4 increases considerably the amount of the TNBA formed, being as high as 95—99% in some experiments. In all cases, the TNT conversion remains sufficiently high (74—80%), and in the presence of H_3BO_3 it reaches 90%. The addition of boric acid is more effective, the more concentrated H_2SO_4 is used for the synthesis. According to the literature data,[17,18] mixing boric acid with concentrated H_2SO_4 affords a very strong acid, namely, tetrahydrosulfatoboric acid $HB(HSO_4)_4$, which provides the significant growth of the acidity of the medium in our case. From the literature data, it follows that an increase in the acidity of the medium due to the presence of this superacid results in acceleration of desulfation of some aromatic amino sulfonic acids[20] as well as in an increase in the effective reaction rate of their isomerization.[21]

Table 1. TNT oxidation with chromic anhydride in sulfuric acid in the presence of boric acid[a]

Entry	$[H_2SO_4]$ (wt. %)	$[H_3BO_3]$ (mol. %)	Conversion (%)	Yield[b] (%)	
				TNBA	PA
1	96	0	80	65	10
2	96	7.3	74	88	2
3	98	0	80	70	—
4	98	1.3	79	74	5
5	98	2.4	85	74	3
6	98	5.8[c]	90	95	1
7	98	8.5[c]	90	88	5
8	100	0	80	81	8
9	100	1.3	89	86	5
10	100	2.8	89	88	4
11	100	5.8	89	88	4
12	100	0.3[d]	88	88	4
13	100	0.6[d]	86	91	2
14	100	0.9[d]	89	99	0.6
15	100	1.1[d]	84	92	0.8

[a] 2,4,6-Trinitrotoluene (2 g), Cr_2O_3 (2.1 g).

[b] Unreacted TNT.

[c] Reaction mixture was kept for 20 h at room temperature after the reaction was accomplished.

[d] Addition of a preliminary prepared solution of $HB(HSO_4)_4$ in 100% H_2SO_4.

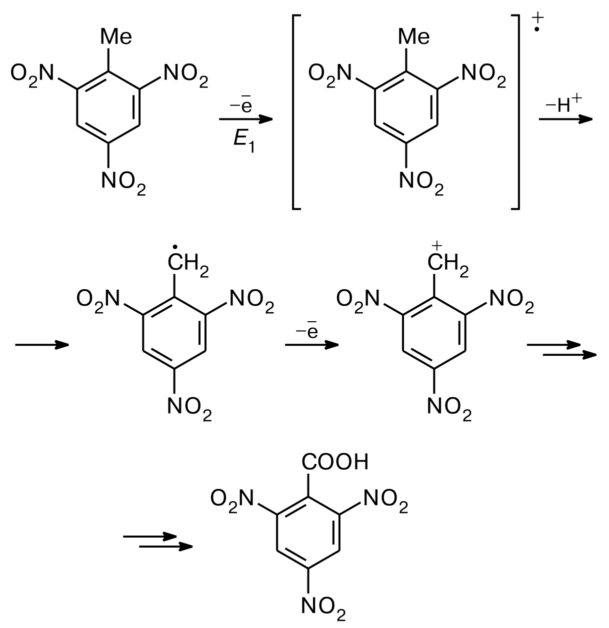
The graph of dependency of the acidity H_0 of the H_2SO_4 solutions in the presence of boric acid *versus* its concentration[18] has a sharp rise just in the area corresponding to 100% H_2SO_4. Experimental data presented in Table 1 correlates with the proposal that at high concentration of H_2SO_4 even minor additives of boric acid considerably increase the TNBA yield. Usage of the preprepared solution of $HB(HSO_4)_4$ in 100% H_2SO_4 proved to be most effective, *i.e.*, under conditions of a nearly complete absence of water in the system.

In all the experiments performed, picric acid (PA) was the side product (up to 10%). Its appearance among the reaction products results probably from the subsequent oxidative transformations of the formed TNBA under "drastic" conditions.[22] Interestingly, the PA content in the reaction products decreases with an increase in the medium acidity. It should be emphasized that no other side products of TNT oxidation were detected. In this case, the losses during isolation of the oxidation products were minimal for high concentrations of H_2SO_4 and also decrease as the concentration of boric acid increased. This result testifies that when E_{ox} is not high enough to effectively oxidaize the TNT methyl group, side reactions can take place, *e.g.,* the cleavage of the aromatic ring followed by the decomposition to CO_2 and H_2O. Therefore, it is necessary to take into account the influence of E_{ox} on the direction and the depth of conversion of compounds resistant to oxidation.

Considering the oxidation mechanism of TNT in terms of the single electron transfer,[1,23] the oxidation reaction can be presented by Scheme 1.

The first step of oxidation of aromatic compounds in most cases presents the formation of a cation radical[1] transforming into the corresponding benzyl radical in the presence of the methyl group capable of eliminating the proton. For TNT, polynitrobenzyl radical should be formed, whose stability is apparently low. The basis for such a hypothesis is provided by quantum chemical calculaitons[24,25] performed for benzylic radicals bearing electron-withdrawing substituents in *para*-position. These calculations allow one to draw a conclusion that such substituents in a ring do not favour the stabilization of benzyl radicals. This fact is also supported by the experimental data. For instance, in a study[26] oxidative dimerization of 4-nitro-, 2,4-dinitro-, and 2,4,6-trinitrotoluenes with

Scheme 1



polynitroalkanes in the presence of bases has been investigated. Being electron acceptors, polynitroalkanes convert anions of polynitroaromatic compounds into the corresponding polynitrobenzyl radicals. The latter are dimerized at the methyl group forming 1,2-substituted ethanes and stilbenes. The yield of dimeric products for 2,4-dinitrotoluene is sufficiently lower than for 4-nitrotoluene. In contrary to 4-nitrotoluene and 2,4-dinitrotoluene, in the presence of sodium *tert*-butoxide TNT decomposes yielding resinous unidentifiable products. Trinitrobenzyl radical formed during the oxidation of the TNT anion under the above conditions is propably insufficiently stable to participate in the dimerization reaction.

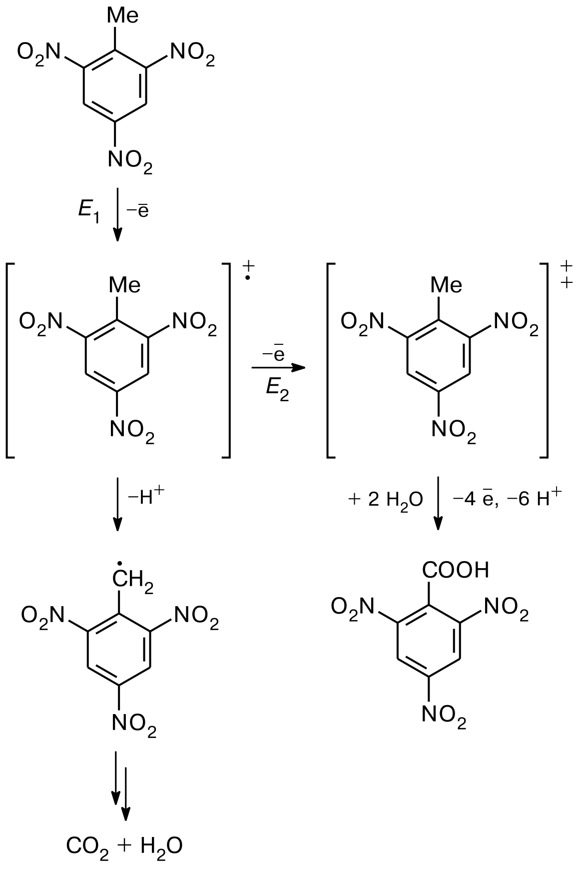
In the study[27] on oxidation of polymethylbenzene nitro derivatives by cyclic voltammetry in superacidic media, it was concluded that fluorosulfonation at the methyl group proceeds following the EEC-mechanism, *i.e.,* the substrate dication reacts with fluorosulfonic acid (a nucleophile) rather than the cation radical.

Considering these data as well as our results on significant increase in TNBA yield under conditions wherein the redox potential of the the oxidation system should be increased, one might propose the mechanism of TNT oxidation (Scheme 2) differing from that depicted on Scheme 1.

Such mechanism (see Scheme 2) explains the role of the redox potential upon oxidation of TNT to TNBA. If the oxidation potential E_{ox} is not high enough for the second electron to be transferred from the cation radical to give the TNT dication ($E_{ox} < E_2$), the labile trinitrobenzyl radical (or cation radical) apparently undergoes a cleavage of the aromatic ring followed by oxidation of intermediates to CO_2 and H_2O. As E_{ox} increases, the rate of formation of TNT dication, which is capable of oxidizing smoothly to TNBA, rises. For the methyl group of TNT to be effectively oxidized, the value of the potential of the second electron transfer should be reached, *i.e.,* the prerequisite of $E_{ox} \geq E_2$ is to be met. Thus, the results obtained on the TNT oxidation provide background to explain the mechanism of the TNT oxidation *via* the formation of a dication rather than a cation radical. Reactivity of dications in electrophilic reactions is known[28,29] to be sufficiently higher than that of monocations. Evidently, it is just this fact that accounts for practically quantitative and selective synthesis of TNBA under conditions favoring the formation of TNT dications. The plausible mechanism of TNT oxidation comprising the formation of a dication as a key reaction species at a specific reaction centre takes place probably also on oxidation of other compounds resistant to oxidation.

To conclude, we have studied the effect of the medium acidity on the yield of TNBA on the TNT oxidation with chromic anhydride in concentrated H_2SO_4 in the presence of boric acid. The yield and selectivity of the TNBA formation increases in the presence of H_3BO_3, as explained by an increase in acidity of the medium due to the formation of $HB(HSO_4)_4$ contributing to the rise of the oxida-

Scheme 2



tion potential of the $Cr_2O_7^{2-}/Cr^{3+}$ system. The effect of the H_3BO_3 additives is observed, when using concentrated (96—100%) solutions of H_2SO_4. Oxidation of TNT proceeds most effectively in solutions practically free of water.

Experimental

Solutions of sulfuric acid of 98 and 100% concentrations were prepared by adding oleum to commercially available sulfuric acid (chemically pure grade). Concentration of H_2SO_4 and oleum was determined by titration with 0.1 *M* NaOH. Solution of tetrahydrosulfatoboric acid was prepared by dissolving boric acid in oleum of the known concentration according to the reaction[18]

$$B(OH)_3 + 3\ H_2S_2O_7 = HB(HSO_4)_4 + 2\ H_2SO_4.$$

2,4,6-Trinitrotoluene was recrystallized from ethanol; H_3BO_3 was dried over conc. H_2SO_4.

Oxidation of TNT was carried out on four-necked flask equipped with a stirrer, a thermometer and a drying tube. To a suspension of TNT (2 g) in H_2SO_4 (11 mL) with a known concentration of H_3BO_3 or its solution in 100% H_2SO_4 was added if required by the experimental conditions. Then CrO_3 (2.1 g) was gradually added and the mixture was maintained for 2 h at 45—55 °C. The reaction mixture was then poured in the glass with ice (15 g). On mixing with ice, the main portion of the TNBA precipitated together with the unreacted TNT. The precipitate was filtered, washed with ice water, dried, and weighted. To determine the yield of TNBA and detect the possible by-products of the reaction, the filtrate was diluted with water (125—150 mL) followed by extraction with ethyl acetate, and the organic compounds dissolved therein were separated from chromium compounds as well as from boric acid. The extract and the precipitate were analysed separately by the ^{1}H NMR spectroscopy and TLC and the amount of the products obtained was calculated according to the ^{1}H NMR spectral data. In some cases TNBA was separated from TNT by dissolving the mixture in an aqueous alkaline solution.[19] Losses of TNBA during purification were 5—7% from its analytically detected amout in the mixture. Melting point of the purified TNBA is 220 °C.

^{1}H NMR spectra were registered on a «Bruker AM-300» spectrometer (working frequency 300 MHz) in $(CD_3)_2CO$ or CD_3OD. Amounts of TNT, TNBA, and PA were calculated from the integral intensities of the corresponding signals of aromatic protons in the ^{1}H NMR spectra.

2,4,6-Trinitrobenzoic acid. ^{1}H NMR (CD_3OD), δ: 9.18 (s, 2 H).

2,4,6-Trinitrophenol (picric acid). ^{1}H NMR (CD_3OD), δ: 8.94 (s, 2 H).

2,4,6-Trinitrotoluene. ^{1}H NMR (CD_3OD), δ: 8.88 (s, 2 H); 3.26 (s, 3 H).

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