ROLE OF NITRONIUM CATIONS AS AN ELECTRON ACCEPTOR IN REACTION OF 2,7-DINITRODIBENZO-1,4-DIOXIN WITH NITRIC ACID

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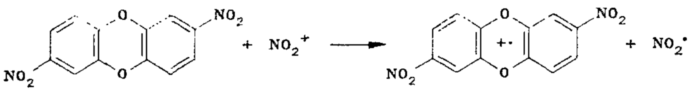
When equal volumes of equimolar solutions ($2 \cdot 10^{-3}$ mole/liter) of 2,7-dinitrodibenzo-1,4-dioxin (I) and nitric acid are mixed together in concentrated sulfuric acid, intensely dark-blue (λ_{max} 658 nm, $D_{658} = 0.9$ at $l = 0.098$ cm) solutions are formed, containing a cation-radical of the substrate. The EPR spectrum of this cation-radical contains 11 equidistant lines with splitting of 0.58 Oe. In the same way as other highly active cation-radicals, radical $I^{+\cdot}$ is readily decomposed by water and is reduced by metals (Cu, Sn), accepting an electron. The disappearance of an absorption band at 658 nm and the appearance of an absorption band of compound I at 374 nm correspond to the latter reaction in the electronic spectrum of the reaction mixture. Manganese oxide can be used instead of nitric acid for the one-electron oxidation of dioxin I.

The oxidation of the nitro derivative I to a cation-radical in the $I-HNO_3-H_2SO_4$ system most probably proceeds by the action of a nitronium cation [1]:



I

$I^{+\cdot}$

$$2\,NO_2^{\cdot} + 2\,H^+ \longrightarrow NO_2^+ + NO^+ + H_2O$$

In fact, in concentrated sulfuric acid, nitric acid is practically completely transformed into a nitronium cation, which is the most reactive oxygenated compound of nitrogen. The rates of reactions of NO_2^+ with many aromatic compounds are determined by the collision frequency of the reagent molecules [2].

The formation of cation-radical of compound I is also readily observed in the reaction of the latter with nitronium tetrafluoroborate in concentrated sulfuric acid or nitromethane.

It is very important to note that it has been found that the nitrosonium cation, which of all the oxygenated nitrogen compounds is inferior only to NO_2^+ in its reactivity towards aromatic compounds, cannot cause a one-electron oxidation of dioxin I under comparable concentration and temperature conditions (cf. [3]). This was ascertained in the study of the action of nitrosonium hydrosulfate or perchlorate solutions in concentrated sulfuric acid on this compound. In this connection, it should be noted that the above examples of one-electron oxidation of heteroaromatic and aromatic derivatives by nitronium tetrafluoroborate [3-5] concern only those compounds which are oxidized to cation-radicals also by nitrosonium cation. We can thus conclude that under the experimental conditions of [3-5], a one-electron oxidation takes place, in particular, by the nitronium cation and not by the nitrosonium cation, which is usually present as an impurity in nitronium salts.

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