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LETTERS TO THE EDITOR

Reactivity of Alkoxy-*NNO*-azoxy Compounds in Potassium Permanganate Aqueous Solution

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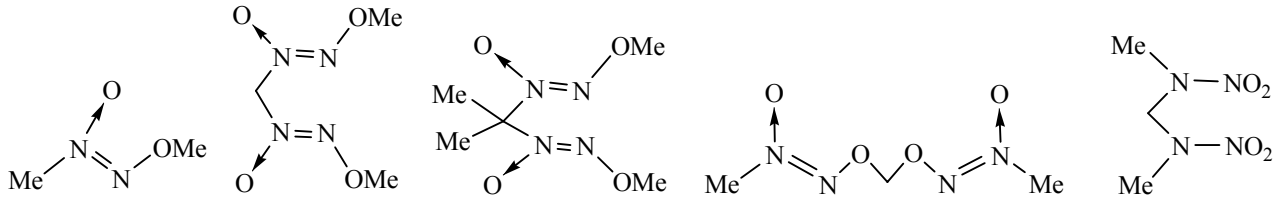
Extending the quantitative study of chemical properties of the alkoxy-*NNO*-azoxy compounds [1–4], we estimated the resistance of model compounds **I**–**IV** and nitramine (structural isomer of **II** and **IV**) **V** to oxidation with potassium permanganate (see Scheme 1).

Compound **I** was almost inert towards oxidization with potassium permanganate in phosphate buffer (pH 1.8) at 20 and 70°C. In the strongly acidic medium (1 M H_2SO_4) at 20°C the reaction did not proceed either; however, at 70°C, concentration of potassium perman-ganate decreased almost linearly, decreasing by 20 times within 4.2 h (from 5×10^{-3} to 0.25×10^{-3} mol/L).

In the alkaline medium, potassium permanganate oxidative properties were enhanced. The time to completely reduce potassium permanganate in 0.2 mol/L NaOH at 20°C with large excess of selected organic compounds was of 7 h (**I**), 10 s (**II**), 7 h (**III**), 6 min (**IV**), 70 h (**V**), 7 min (MeOH), 4 h (Et_2O); without any organic component (reference experiment) the reduction took 200 h. Compound **II** was oxidized most rapidly, due to acidic properties of the central H atoms of the molecule. That was confirmed by 2500 times higher resistance in the case of compound **V** (in the latter, the acidic H atoms were replaced with Me groups). As followed from comparison of the measured $KMnO_4$ reduction time in the case of **II** (10 s at 20°C) with the hydrolysis rate of **II** in 5 mol/L KOH solution at 80°C ($k_{1,ef}$ of 1.12×10^{-4} s^{-1}) [1], anion of **II** was relatively stable towards alkaline hydrolysis, being easily oxidized with permanganate. The close resistance to oxidation of compounds **I**, **III**, and Et_2O suggested that the oxidation mechanism should involve MeO groups. Furthermore, nitramine **V**, containing no C–O bonds, was an order of magnitude more stable than compounds **I** and **III**, whereas compound **IV** with the geminal C–O bonds was 70 times less stable.

The study of relative resistance of alkoxy-*NNO*-azoxy compounds to oxidation is important to develop new synthetic approaches involving compounds of that class. In particular, potassium permanganate in the alkaline medium was not suitable for oxidative modification of the functional groups of geminal bis-alkoxy-*NNO*-azoxy compounds containing H atoms at the central carbon atom due to its low oxidative resistance under those conditions.

Scheme 1.



Determination of resistance to oxidation. Solution of the respective compound **I–V** (0.1 mol/L, 10 mL, 1 μmol) was added to $KMnO_4$ solution (0.02 mol/L, 10 mL, 0.2 μmol) in 20 mL of 2 mol/L H_2SO_4 or in phosphate buffer (pH 1.8). The mixture was sampled at regular intervals (2 mL), the specimen was diluted with phosphate buffer, and excess of KI solution was added to it. The resulting mixture was titrated with standard $Na_2S_2O_3$ solution to estimate the residual permanganate concentration. To determine the compounds resistance to oxidation in the alkaline medium, 1 mL of 0.02 mol/L solution of $KMnO_4$ and 1 mL of 2 mol/L NaOH was added to solution of the respective compound (**I–V**, MeOH, Et_2O) (0.1 mmol) in 8 mL of water at 20°C. Change of the mixture color from pink to green reflected the reaction completed.

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