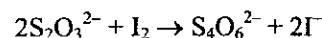


# Answers

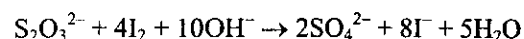
## 2002

1. Equation of the reaction occurring during titration:

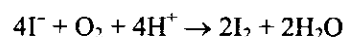


3. Metallic iodine can precipitate if no excess of iodide is added to the analyzed iodine solution.

4. The titration should be carried out in neutral or weakly acidic medium. A side reaction occurs in *alkaline* medium (pH 10):



- The stoichiometry of this reaction differs from that of the main titration reaction. Iodide ions are partially oxidized by air oxygen in *strongly acidic* medium:



Titration can be carried out in weakly acidic medium (till ca. pH 3).

8. The optimal system provides  $R_f$  values around 0.5.

10. The melting point of the product reported in literature is 112 – 113 °C.

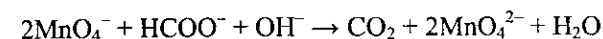
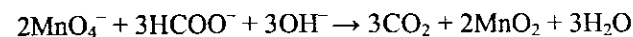
11. The group of multiplets with the total integral intensity of 10 corresponds to the protons of two benzene rings. The singlet at about 4.75 ppm with the integral intensity of about 4 (integral intensities of signals in NMR spectra are typically rounded, since the values are measured with an error of about 5–10%) corresponds to the protons of benzyl groups. To attribute the remaining signals let us analyze the structure of the obtained compound, multiplicity and integral intensities of the rest signals. The  $\text{ICH}_2$  group is found next to the CH fragment, which, in turn, is close to the methylene group of the heterocycle. There are four groups of signals in the range from 3.7 to 4.6: two proton doublet at 3.70 ppm with the constant of spin-spin coupling of  $300 \cdot (3.714 - 3.692) = 7$  Hz (after rounding), two doublets of doublets: at 3.91 ppm with spin-spin coupling constants of 12 and 3 Hz and at 4.18 ppm, 12 and 7 Hz; one proton multiplet at 4.51 ppm. Analysis of spin-spin coupling constants and integral intensities of the signals suggests that the signal at 3.70 ppm referring to the  $\text{ICH}_2$  group is splitted into a doublet at the neighboring methylene group; the doublets of doublets at 3.91 and 4.18 ppm correspond to the methylene group of the heterocycle. Finally, the multiplet at 4.51 ppm corresponding to the methine proton is simultaneously splitted at neighboring methylene groups.

## 2003

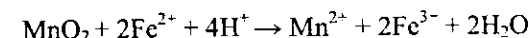
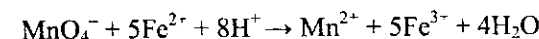
1.  $\text{HCOOH} + \text{OH}^- \rightarrow \text{HCOO}^- + \text{H}_2\text{O}$

2. The concentration of formic acid ( $c_{\text{HCOOH}}$ , mol/L) is calculated as:  $c_{\text{HCOOH}} = c_{\text{NaOH}} V_{\text{NaOH}} / V_{\text{HCOOH},1}$ .

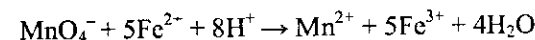
3. As it is mentioned in the task, permanganate can be reduced to both manganese dioxide and manganese as a result of formate oxidation in soda solution:



4. Both excessive  $\text{MnO}_4^-$  and  $\text{MnO}_2$  formed as a result of formate oxidation are reduced when Mohr's salt interacts with the acidified solution obtained after formate oxidation:



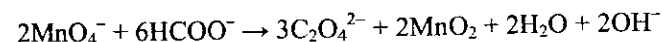
5. Mohr's salt titration with permanganate proceeds stoichiometrically:



6. Finally, the formic acid concentration in the analyzed solution can be calculated as:

$$c_{\text{HCOOH}} = (5V_{\text{Mn},1} c_{\text{Mn},1} + 5V_{\text{Mn},2} c_{\text{Mn},2} - V_{\text{Fe}} c_{\text{Fe}}) / 2V_{\text{HCOOH}}$$

7. Of the reactions given, only incomplete formate oxidation leading to the oxalate ion (see the introduction to the task) can affect the accuracy of the formic acid determination:



Permanganate reduction to manganese dioxide (instead of  $\text{MnO}_4^{2-}$ ) has no effect, since both  $\text{MnO}_4^-$  and  $\text{MnO}_2$  are reduced after acidification and  $\text{Fe}^{2+}$  addition (see above). Other reactions (1, 3–5) are impossible under the titration conditions.

8. The  $R_f$  value is about 0.5 in the optimal system.

14. The literature melting point is 172 – 173 °C.