KINETICS OF SOME FLUOROQUINOLONES OXIDATION BY PERMANGANATE IONS IN BASIC MEDIUM

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Fluoroquinolones are synthetic antibacterial agents of broad action spectrum for peroral administration. Because of heavy use, fluoroquinolones get into the environment through waste waters, biomass, compost, animal waste and they can cause serious harm to flora and fauna of water reservoirs even at their extremely low concentrations. Development of improved methods of fluoroquinolones oxidation, leading to their transformations in aqueous medium, is an important task of modern chemistry.

In present work there has been studied the kinetics of oxidation of two fluoroquinolones (FQ) antibiotics representatives – ofloxacin (OF) and ciprofloxacin (CF) by MnO_4^- ions in aqueous solutions in basic medium. There was used photometric method, with the aid of which there was measured the absorbance of reaction mixture at different time points, at λ = 525 nm, corresponding to maximum of permanganate ions absorption.

According to the low of mass action, the reaction rate of both reactions can be expressed as follows:

$$r = k[MnO_4^-]^{n_1}[FQ]^{n_2}[OH^-]^{n_3}, \qquad (1)$$

where k is the reaction rate constant; n_1 , n_2, n_3 –reaction orders on MnO_4^-, FQ (OF or CF) and OH^-, correspondingly.

If $[MnO_4^-]_0 \ll [FQ]_0$ and $[MnO_4^-]_0 \ll [OH^-]_0$, then it can be considered that during the reaction [FQ] = const and $[MnO_4^-] = const$ and equation (1) can be written as

$$r = k_{obs}[MnO_4^-]^{n_1}, \qquad (2)$$

where k_{obs} is the observed constant, equal to

$$k_{obs} = k[FQ]^{n_2}[OH^-]^{n_3} \qquad (3)$$

For the determination of the reaction orders on MnO_4^- ions, each of both reactions was carried out at five different initial concentrations of MnO_4^- and constant concentrations of FQ and OH^- providing that $[MnO_4^-]_0 \ll [FQ]_0$ and $[MnO_4^-]_0 \ll [OH^-]_0$. On the basis of the obtained data there were plotted dependences $\ln(A_t - A_\infty) = f(t)$ (A_t, and A_∞ - the absorbance of the reaction mixture at the time t, and, respectively, residual absorbance), which presented straight lines with negative slope, consequently it was concluded that the reaction order on MnO_4^- ions was equal to $n_1 = 1$ in the case of both antibiotics.

For the determination of the reaction orders on OF, CF and OH^- ions, the reactions were carried out at constant concentration of MnO_4^- and different concentrations of OF, OH^- and CF, OH^- (providing that $[MnO_4^-]_0 \ll [FQ]_0$ and $[MnO_4^-]_0 \ll [OH^-]_0$). From graphic dependences $\ln(A_t - A_\infty) = f(t)$ there were determined the values of the observed constant k_{obs}. On the basis of the obtained data there were plotted graphic dependences $lg\, k_{obs} = f([OF])$, $lg\, k_{obs} = f([CF])$ and $lg\, k_{obs} = f([OH^-])$, and from the slope of the obtained straight lines there were determined the reaction orders on OF, CF and OH^- ions.

It has been determined that in the case of OF oxidation the reaction order on OF is $n_2 = 0,62$ and the reaction order on OH^- is $n_3 = 0,18$.

In the case of CF oxidation it has been determined that the reaction orders on CF and OH^- are also less than 1.