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SUPPLEMENTARY INFORMATION

KINETIC STUDY OF AN AUTOCATALYTIC REACTION: NITROSATION OF FORMAMIDINE DISULFIDE

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The rate of the nitrosation process is given by the equation 1.

$$r = k_{NO^+}K_{NO^+}K_a^I[\mathrm{HNO_2}][\mathrm{FDSH_2^{2+}}] + k_{NOSCN}K_{NOSCN}K_a^I[\mathrm{FDSH_2^{2+}}][\mathrm{SCN^-}][\mathrm{HNO_2}] \quad (1)$$

In all cases the condition (2) is fulfilled and $[\mathrm{FDSH_2^{2+}}] \cong [\mathrm{FDSH_2^{2+}}]_0$, the amount of thiocyanate ion is given by (3), using (4) and (5) simplifies equation (1) to (6).

$$[\mathrm{FDSH_2^{2+}}] >> [\mathrm{HNO_2}] \quad (2)$$

$$[\mathrm{SCN^-}] = 5/6\left([\mathrm{HNO_2}]_0 - [\mathrm{HNO_2}]\right) \quad (3)$$

$$k_1 = k_{NO^+}K_{NO^+}K_a^I[\mathrm{FDSH_2^{2+}}]_0 \quad (4)$$

$$k_2 = k_{NOSCN}K_{NOSCN}K_a^I[\mathrm{FDSH_2^{2+}}]_0 \quad (5)$$

$$r = k_1[\mathrm{HNO_2}] + 5/6k_2[\mathrm{HNO_2}]\left([\mathrm{HNO_2}]_0 - [\mathrm{HNO_2}]\right) \quad (6)$$

Equation (6) is reorganized to (7), by applying (8) the rate equation can be rewritten as (9). The integrated equation is (11).

$$r = -\frac{d[\mathrm{HNO_2}]}{dt} = \left(k_1 + 5/6k_2[\mathrm{HNO_2}]_0\right)[\mathrm{HNO_2}] - 5/6k_2[\mathrm{HNO_2}]^2 \quad (7)$$

$$k_3 = k_1 + 5/6k_2[\mathrm{HNO_2}]_0 \quad (8)$$

$$r = -\frac{d[\mathrm{HNO_2}]}{dt} = k_3[\mathrm{HNO_2}] - 5/6k_2[\mathrm{HNO_2}]^2 \quad (9)$$

$$-\int_{[HNO_2]_0}^{[HNO_2]} \frac{d[\mathrm{HNO_2}]}{k_3[\mathrm{HNO_2}]-5/6\,k_2[\mathrm{HNO_2}]^2} = \int_0^t dt \tag{10}$$

$$[\mathrm{HNO_2}] = \frac{k_3[\mathrm{HNO_2}]_0}{\left(k_3-5/6\,k_2[\mathrm{HNO_2}]_0\right)e^{k_3 t}+5/6\,k_2[\mathrm{HNO_2}]_0} \tag{11}$$

The reaction kinetics were studied at 370 nm by following the disappearance of HNO_2. Considering A_t, A_∞ and A_0 as the measured absorbances at time *t*, at the end of the reaction and at the beginning of reaction, respectively, we obtain the expression (15).

$$\left(A_t - A_\infty\right) = \varepsilon \times \ell \times [\mathrm{HNO_2}] \tag{12}$$

$$\left(A_0 - A_\infty\right) = \varepsilon \times \ell \times [\mathrm{HNO_2}]_0 \tag{13}$$

$$\varepsilon' = \varepsilon \times 1\ \mathrm{cm} \tag{14}$$

$$A_t = A_\infty + \frac{\varepsilon' k_3\left(A_0 - A_\infty\right)}{\left[\varepsilon' k_3 - 5/6\,k_2\left(A_0 - A_\infty\right)\right]e^{k_3 t} + 5/6\,k_2\left(A_0 - A_\infty\right)} \tag{15}$$

When a halide anion X^- is present in the reaction medium a new contribution to the rate must be added to equation (1) giving equation. When considering (17) equation (16) gives (18) that can be reorganized into equation (21).

$$r = k_{NO^+}K_{NO^+}K_a^I[\mathrm{HNO_2}][\mathrm{FDSH_2^{2+}}] + k_{NOSCN}K_{NOSCN}K_a^I[\mathrm{FDSH_2^{2+}}][\mathrm{SCN^-}][\mathrm{HNO_2}] + k_{NOX}K_{NOX}K_a^I[\mathrm{FDSH_2^{2+}}]_0[\mathrm{X^-}]_0 \tag{16}$$

$$k_4 = k_{NOX}K_{NOX}K_a^I[\mathrm{FDSH_2^{2+}}]_0[\mathrm{X^-}]_0 \tag{17}$$

$$r = k_1[\mathrm{HNO_2}] + k_2\left(5/6\left([\mathrm{HNO_2}]_0 - [\mathrm{HNO_2}]\right)\right)[\mathrm{HNO_2}] + k_4[HNO_2] \tag{18}$$

$$r = -\frac{d[\mathrm{HNO_2}]}{dt} = \left(k_1 + 5/6\,k_2[\mathrm{HNO_2}]_0 + k_4\right)[\mathrm{HNO_2}] - 5/6\,k_2[\mathrm{HNO_2}]^2 \tag{19}$$

$$k_5 = \left(k_1 + k_2\left(5/6[\mathrm{HNO_2}]_0\right) + k_4\right) \tag{20}$$

$$r = -\frac{d[\mathrm{HNO_2}]}{dt} = k_5[\mathrm{HNO_2}] - 5/6\,k_2[\mathrm{HNO_2}]^2 \qquad (21)$$

The expression (21) is formally equivalent to (9) and can be integrated giving the expression (22). The late equation can be expressed as function of the absorbance by equation (23).

$$[\mathrm{HNO_2}] = \frac{k_5[\mathrm{HNO_2}]_0}{\left(k_5 - 5/6\,k_2[\mathrm{HNO_2}]_0\right)e^{k_3 t} + 5/6\,k_2[\mathrm{HNO_2}]_0} \qquad (22)$$

$$A_t = A_\infty + \frac{\varepsilon' k_5\left(A_0 - A_\infty\right)}{\left[\varepsilon' k_5 - 5/6\,k_2\left(A_0 - A_\infty\right)\right]e^{k_3 t} + 5/6\,k_2\left(A_0 - A_\infty\right)} \qquad (23)$$