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THE OXIDATION OF *o*-BENZOQUINONE DIOXIME BY $[Fe(CN)_6]^{3-}$ AND THE EVALUATION OF OXIME K_{a1}

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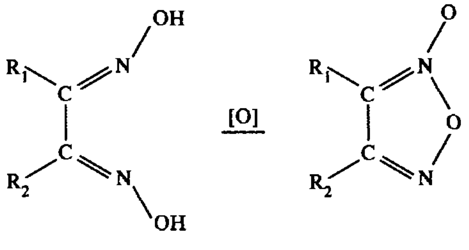
Abstract—The kinetics of the oxidation of *o*-benzoquinone dioxime (DOX-H_2) by hexacyanoferrate(III) in a buffered alkaline aqueous methanolic medium have been studied spectrophotometrically. A rate dependence on the dioxime, the oxidant and OH^- concentrations has been found:

$$-d[\text{DOX-H}_2]/dt = k_{obs}[\text{DOX-H}_2][Fe(CN)_6{}^{3-}][OH^-].$$

The rate measurements were used to calculate the thermodynamic activation parameters $\Delta G^\ddagger$, $\Delta H^\ddagger$, $\Delta S^\ddagger$ and K_{a1} of *o*-benzoquinone dioxime.

Many α-diketone dioximes (**I**) are known for their important role in analytical and inorganic chemistry.[1] However, little is known about their redox properties. In fact, they are considered as intermediates, in their oxidation states, between α-diamines and furoxans (**II**).[2] Thus, α-diketone dioximes have been oxidized via chemical[3] or electrochemical[4] methods to give the corresponding benzofuroxans (BFO). Yet, there has been no kinetic study of the oxidation of α-diketone dioxime into furoxans. In line with our interest in the kinetic oxidation of α-hydroxy ketones,[5] we report here on the kinetic oxidation of *o*-benzoquinone dioxime and the use of kinetic data to evaluate the first acid dissociation constant (K_{a1}) of that dioxime in 50% aqueous methanol.



I   II

EXPERIMENTAL

Materials

The *o*-benzoquinone dioxime was prepared by the reduction of benzofuroxan via hydrazobenzene[6] and purified by sublimation. $K_3[Fe(CN)_6]$ used in this investigation was B.D.H. Analar grade, and was used without further purification. Analytical grade reagents and doubly distilled water were used throughout the measurements. The desired buffer solutions for varying pH of the reaction medium were prepared by mixing suitable volumes of 0.050 M sodium bicarbonate and 0.10 M NaOH. The pH was measured with a Metrohm 632 pH meter. The measured pH values were corrected for 50% v/v aqueous methanol using the relationship:[7] $pH_{corr} = pH_{meas}+0.08$.

Kinetic measurements

The oxidation reactions were carried out in a buffered alkaline aqueous methanol (50% v/v) using a thermostated bath to regulate the temperature to ±0.2°C. The ionic strength was adjusted to a constant value of 0.05 M by the

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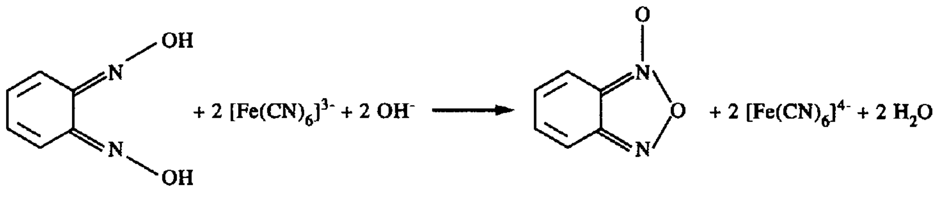
addition of NaCl. Kinetic data were obtained by monitoring the decrease in the concentration of *o*-benzoquinone dioxime anion at 460 nm with a thermostated Unicam SP8-500 spectrophotometer.

Stoichiometry

The oxidation of *o*-benzoquinone dioxime (**III**) with $K_3[Fe(CN)_6]$ was found to proceed by a 1 : 2 stoichiometry represented in the following equation:



III **IV**

The formation of benzofuroxan (BFO, **IV**) was followed by monitoring its absorption at 350 nm.

RESULTS AND DISCUSSION

Effect of o*-benzoquinone dioxime*

Absorption measurements were carried out at 25°C and at pseudo-first order kinetics: $[Fe(CN)_6^{3-}] = 2.0 \times 10^{-3}$M, [*o*-benzoquinone dioxime] = 1.0×10^{-4}], pH = 10.0, and at a constant ionic strength of 0.050 M. The decrease in the concentration of *o*-benzoquinone dioxime anion was monitored by measuring the absorbance (A) at 460 nm. A plot of $\ln A$ vs t gave a straight line indicating first-order kinetics with respect to the *o*-benzoquinone dioxime.

Effect of $[Fe(CN)_6]^{3-}$

Absorption measurements were carried out at stoichiometric molar ratios of the reactants (*o*-benzoquinone dioxime : oxidant ratio, 1 : 2) and at different pH values. The plots of $1/A_t$ vs t are linear (Fig. 1), indicating a first-order dependence on both the *o*-benzoquinone dioxime and $[Fe(CN)_6]^{3-}$ concentrations. Thus the rate can be expressed as shown in the following equation:

$$-d[DOX\text{-}H_2]/dt = k[DOX\text{-}H_2][Fe(CN)_6]^{3-}].$$

Effect of pH

From the above kinetic measurements carried out at stoichiometric molar ratios, showing the rate dependence on the oxidant concentration, values of the rate constant, k ($M^{-1}\ s^{-1}$) were evaluated (Table 1). Plot of log k vs pH gave a straight line with a slope of 0.97, indicating a first-order dependence on $[OH^-]$. Accordingly, the overall rate can be expressed as shown in the following equation:

$$-d[DOX-H_2]/dt = k_{obs}[DOX\text{-}H_2][[Fe(CN)_6]^{3-}][OH^-].$$

Consistent with the above kinetic data, the following mechanism for the oxidation of *o*-benzoquinone dioxime ($DOX\text{-}H_2$) is proposed:

$$DOX\text{-}H_2 + OH^- \overset{K}{\rightleftharpoons} DOX\text{-}H^- + H_2O \quad (1)$$

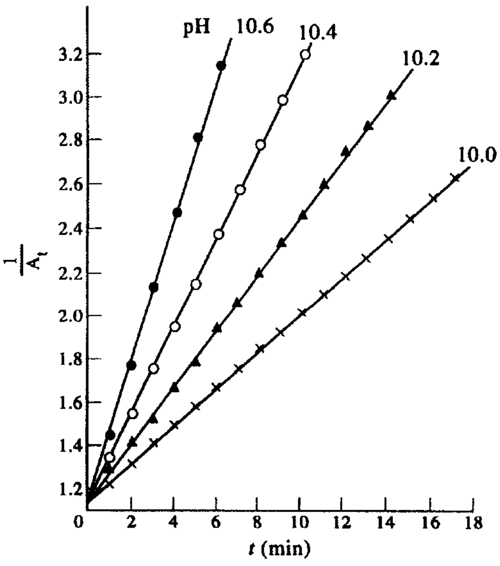


Fig. 1. Plots of $1/A_t$ vs time for the oxidation of *o*-benzoquinone dioxime by $[Fe(CN)_6]^{3-}$ at different pH values.

Table 1. Effect of pH on reaction rate[a]

pH	k ($dm^3\ mol^{-1}\ s^{-1}$)
10.0	8.08
10.2	11.4
10.4	17.4
10.6	29.1
10.8	41.8
11.0	63.0

[a] [Dioxime] = 2.0×10^{-4} M, $[Fe(CN)_6^{3-}] = 4.0 \times 10^{-4}$ M, T = 25.0°C, I = 0.050 M.

$$DOX\text{-}H^- + [Fe(CN)_6]^{3-} \xrightarrow{k_2} DOX\text{-}H^{\bullet} + [Fe(CN)_6]^{4-} \quad (2)$$

$$DOX\text{-}H^{\bullet} + [Fe(CN)_6]^{3-} + OH^- \xrightarrow{FAST} DOX + [Fe(CN)_6]^{4-} + H_2O \quad (3)$$

$$DOX \xrightarrow{FAST} BFO. \quad (4)$$

Assuming that step (2) is the rate determining step, the following third-order rate law is derived

$$-d[DOX\text{-}H_2]/dt = k_2K[DOX\text{-}H_2][[Fe(CN)_6]^{3-}][OH^-]$$

where $k_{obs} = k_2K$.

Thermodynamic parameters

The enthalpy of activation was evaluated upon variation of the reaction temperature between 15 and 30°C under second-order conditions ($[DOX-H_2] = 2.0 \times 10^{-4}$ M, $[Fe(CN)_6^{3-}] = 4.0 \times 10^{-4}$ M) at constant pH (10.0) and constant ionic strength (0.050 M). Plots of $-\log(k/T)$ vs $1/T$ gave a straight line. The value of $\Delta H^{\ddagger}$ was obtained from the slope and the values of $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ were calculated at 25°C. $\Delta H^{\ddagger} = 46.5$ kJ mol^{-1}, $\Delta S^{\ddagger} = -194\ J\ K^{-1}\ mol^{-1}$ and $\Delta G^{\ddagger} = 104\ kJ\ mol^{-1}$.

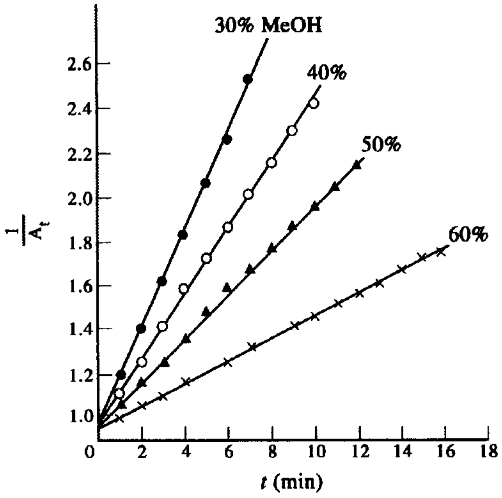


Fig. 2. Plots of $1/A_t$ vs time for the oxidation of *o*-benzoquinone dioxime by $[Fe(CN)_6]^{3-}$ at different solvent composition.

Solvent effect

Kinetic measurements were carried out at a stoichiometric molar ratio of the reactants (oxidant : dioxime ; 2 : 1) at 25°C, pH = 10.0, and at constant ionic strength (0.050 M) in aqueous methanolic solutions with methanol compositions of: 30%, 40%, 50% and 60% v/v. From the plots of $1/A_t$ vs t (Fig. 2) for each solvent composition, the values of the rate constant were obtained (Table 2). The data in Table 2 shows that the rate constant increases with increasing dielectric constant (D). The relationship between ln k and D is given by the following equation :

$$\ln k = \ln k_{\infty} - \frac{Z_A Z_B e^2}{DkTd_{AB}}$$

where Z_A and Z_B are the monooxime anion charge (−1) and the oxidant anion charge (−3), respectively; d_{AB} is the distance of closest approach between reacting species.

A plot of ln k vs $1/D$ gave a straight line, from which the value of d_{AB} has been obtained and found to be 412 pm.

K_{a1} *of* o*-benzoquinone dioxime*

The acid dissociation constant (K_a) of some weak acids (e.g. indicators) could be evaluated spec-

Table 2. Effect of dielectric constant of the solvent on the reaction rate[a]

%Methanol	D_{25}	k ($M^{-1}\ s^{-1}$)	ln$k$	$1/D_{25}$
30	67.50	19.73	2.98	1.481
40	63.25	12.96	2.56	1.581
50	58.72	8.08	2.09	1.702
60	54.28	4.52	1.51	1.842

[a] [Dioxime] = 2.0×10^{-4} M, $[Fe(CN)_6]^{3-} = 4.0 \times 10^{-4}$ M, T = 25.0°C, I = 0.050 M.

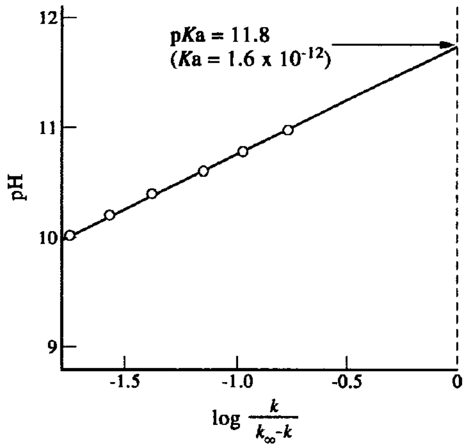


Fig. 3. Plots of pH vs log $k/(k_\infty - k)$ for the oxidation of *o*-benzoquinone dioxime by $[Fe(CN)_6]^{3-}$.

trophotometrically[8,9] using the following relationship:

$$pK_a = pH - \log\frac{[A^-]}{[HA]} = pH - \log\frac{A - A_a}{A_b - A}$$

where A is the absorbance of the solution at a specific pH, A_a and A_b are the corresponding absorbances of the same concentration solution in acid and alkaline solution. In this study the acid first dissociation constant of the *o*-benzoquinone dioxime was evaluated from kinetic measurement, using the following equation:

$$pK_a = pH - \log\frac{k - k_a}{k_b - k} \qquad (5)$$

where k is the rate constant measured at a specific pH in the range 10.0–11.0, k_a is the rate constant in highly acidic medium, and k_b is the rate constant in highly basic medium (100% ionization). In such conditions $k_a = 0$ and $k_b = k_\infty$ and eq. (5) is reduced to:

$$pK_a = pH - \log\frac{k}{k_\infty - k}. \qquad (6)$$

Solving eq. (6) at two different pH values allows the calculation of k_∞ which is found to be 4.6×10^2 M^{-1} s^{-1}. A plot of pH vs $\log[k/(k_\infty - k)]$ gave a straight line (Fig. 3), from which the value of K_{a1} was calculated and found to be 1.6×10^{-12}.

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