

Kinetics and Oxidation of Nitrite Ion by Quinolinium Dichromate

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Abstract: The kinetics of oxidation of nitrite ion by quinolinium dichromate in perchloric acid medium is studied. A stoichiometric ratio of 3:1 with nitrite vs. QDC was observed. The reaction is first order with respect to [QDC] and [H⁺] and second order behavior with respect to [nitrite]. The mechanism involved the attack of protonated monomeric QDC (HQMC) on the substrate in the rate determining step forming a cyclic ester type complex which subsequently yielded the products. A suitable mechanism is proposed.

Keywords: monomeric quinolinium dichromate (QMC), nitrite, oxidation, effect of anionic and neutral micelle.

I. INTRODUCTION

The aqueous solution chemistry of nitrous acid and nitrites by chromium (VI) has been extensively studied^{1,2}. Nitrites are quantitatively oxidized to nitrate by various oxidizing agents which include iodine³, bromine⁴, chlorine⁵, hypochlorites, chlorites^{6,7}, hypobromite⁸, hydrogenperoxide⁹, chromium(VI)¹⁰, vanadium (V)¹¹, manganese (VII)^{12,13} and manganese(III)¹⁴ as well as diamino cyclohexane tetraacetato manganese (III)¹⁵. The kinetics of electro chemical oxidation of nitrous acid¹⁶ has also been studied. It is interesting to study the kinetic features when quinolinium moiety is incorporated in HCrO₄⁻. Hence, the author has taken up the kinetic study of oxidation of nitrite ion by quinolinium dichromate (QDC) in aqueous perchloric acid medium to find out any mechanistic and kinetic differences compared to the oxidation by aqueous chromium (VI).

II. EXPERIMENTAL

Materials:

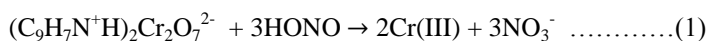
All the chemicals were of high grade quality and were used as received without further purification. Quinolinium dichromate (QDC) was prepared by the reported method¹⁷ and standardized¹⁸. Its purity was checked by spectral analysis. The infrared spectrum (KBr) exhibited bands at 930, 875, 765 and 730 cm⁻¹, characteristic of the dichromate ion. 0.1 mol dm⁻³ solution of sodium nitrite was prepared by dissolving a requisite amount in a known volume of water. The solution was standardized by the procedure described in Vogel¹⁹. Sodium perchlorate (Fluka) and perchloric acid were used without purification and enabled variation of hydrogen ion concentration at a constant ionic strength (1.0M).

Kinetic measurements:

The reaction was followed by measuring the optical density of the unreacted QDC at 440 nm using Perkin Elmer Lambda 25 UV/ VIS spectrophotometer. The experiments were carried out in a temperature controlled ($\pm 0.1^{\circ}\text{C}$) water bath. The reaction was initiated by adding, QDC (2.0×10^{-3} mol dm⁻³) with nitrite (2.0×10^{-2} mol dm⁻³) and perchloric acid (1.0 mol dm⁻³) mixture at an ionic strength of 0.25 mol dm⁻³ using sodium perchlorate at 303K. The reaction is monitored by determining the absorbance at different times and log (absorbance) vs. time plots are perfectly linear for at least 95% of the reaction. Beer's law is strictly obeyed for all the reactant concentrations. The pseudo first order constants determined in duplicate agreed within $\pm 5\%$.

Stoichiometry:

To determine the stoichiometry of the reaction a known concentration of nitrite was mixed with different concentrations of QDC at $[H^+] = 1.0 \text{ mol dm}^{-3}$ in water. The reaction mixtures were kept overnight for the completion of the reaction and the absorbance was measured at 440nm. It was found that three moles of nitrite ion requires one mole of QDC.



III. RESULTS

Effect of varying [QDC], [acid] and $[NO_2^-]$ on the rate of reaction:

Kinetic runs were carried out by varying [QDC], under the conditions of $[QDC] \ll [NaNO_2]$. Plots of log (absorbance) vs. time were found to be linear for at least 95% of the reaction, showing the first order kinetics with respect to QDC. The pseudo – first order rate constants k_1 calculated from the slopes of these plots are given in Table .1. The straight line graphs obtained at different concentrations of QDC were found to be parallel to each other, which further confirm the pseudo first order kinetics with respect to QDC.

Kinetic runs were carried out at different $[H^+]$ in the range (0.2 to 1.2) mol dm^{-3} keeping the concentration of QDC and NO_2^- constant at 303K. The ionic strength was maintained constant with $NaClO_4$.The plot of k_1 vs. $[H^+]$ was found to be linear passing the origin showing the first order kinetics with respect to $[H^+]$ is presented in Table 1.

To determine the effect of $[NO_2^-]$ on the rate, the kinetic runs were carried out at different $[NO_2^-]$ in the range (0.5 – 4.0) $\times 10^{-2} \text{ mol dm}^{-3}$, keeping the $[H^+]$ and [QDC] constant at 303K. The plot of k_1 versus $[NO_2^-]$ is concave upwards showing that the order with respect to NO_2^- is greater than unity. However a plot (Figure 1) of $k_1/[NO_2^-]$ vs. $[NO_2^-]$ is linear with a positive intercept. This shows that the rate law is the sum of two terms, corresponding to the different rate determining steps in the reaction and is second order with respect to NO_2^- . The result can be represented by the empirical relation $k_1 = a[NO_2^-] + b[NO_2^-]^2$.

Table 1 : Effect of variation of $[NO_2^-]$, [QDC], $[H^+]$ on the oxidation kinetics of nitrite by quinolinium dichromate at 303K and $I = 0.25 \text{ mol dm}^{-3}$

$[QDC]10^3$ mol dm^{-3}	$10^2[NO_2^-]$ mol dm^{-3}	$[H^+]$ mol dm^{-3}	10^3k_1 sec^{-1}
1.0	1.0	1.0	2.98 ± 0.3
1.5	1.0	1.0	3.23 ± 0.2
2.0	1.0	1.0	3.14 ± 0.3
2.5	1.0	1.0	3.32 ± 0.4
3.0	1.0	1.0	2.99 ± 0.2
3.5	1.0	1.0	3.18 ± 0.3
2.0	0.5	1.0	1.12 ± 0.4
2.0	1.0	1.0	3.14 ± 0.5
2.0	2.0	1.0	9.60 ± 0.4
2.02	2.5	1.0	14.90 ± 0.2
2.0	3.0	1.0	20.00 ± 0.3
2.0	4.0	1.0	33.58 ± 0.4
2.0	1.0	0.2	0.63 ± 0.3
2.0	1.0	0.4	1.31 ± 0.4
2.0	1.0	0.6	1.94 ± 0.3
2.0	1.0	0.8	2.59 ± 0.2
2.0	1.0	1.0	3.23 ± 0.3
2.0	1.0	1.2	3.91 ± 0.4

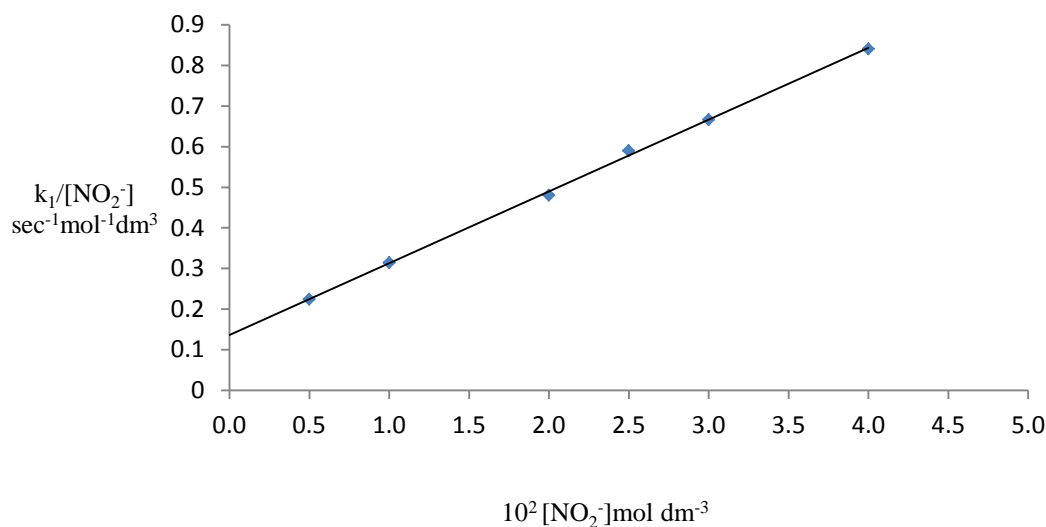


Figure 1: Plot of $k_1/[\text{NO}_2^-]$ vs. $[\text{NO}_2^-]$ at $[\text{QDC}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$; $\mu = 0.25 \text{ mol dm}^{-3}$; $\text{Temp} = 30^0 \text{c} \pm 0.1^0 \text{c}$

Activation parameters:

The values of k_1 were determined at different temperatures and the apparent activation energy from the data has been obtained. The values of activation parameters were calculated to be $E_a = 38.294 \text{ KJ / mol}$, $\Delta H = 35.775 \text{ JK}^{-1} \text{ mol}^{-1}$, $\Delta S = -183.16 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\Delta G = 91.2736 \text{ KJ}$.

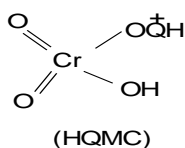
IV. DISCUSSION

Kinetic approach:

The plot of $k_1/[\text{NO}_2^-]$ vs. $[\text{NO}_2^-]$ is a straight line with a very well defined intercept which is presumably the decomposition of the 1:1 intermediate. The pseudo first order rate constant, k_1 , must be therefore related to $[\text{NO}_2^-]$ by the empirical rate:

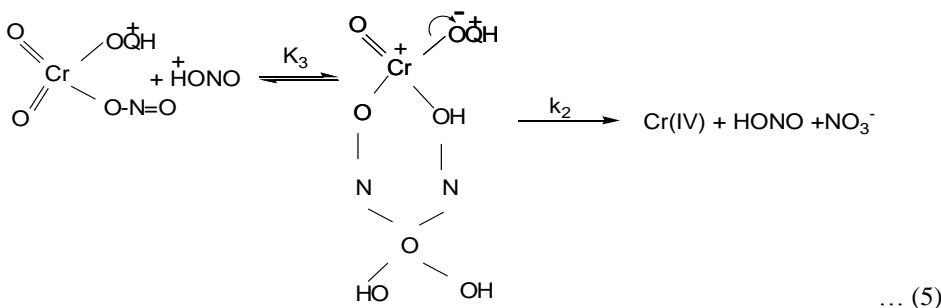
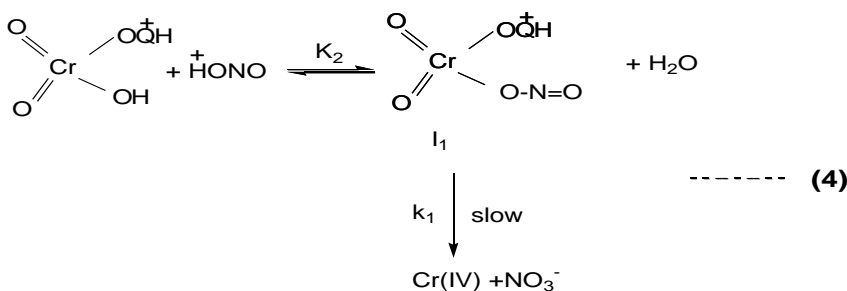
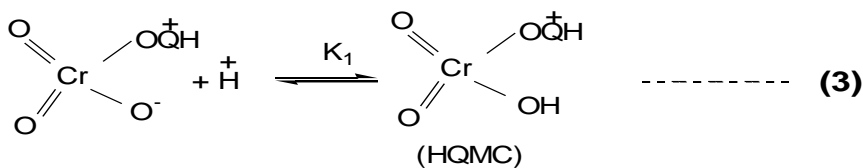
$$k_1 = a [\text{NO}_2^-] + b [\text{NO}_2^-]^2 \dots\dots\dots (2)$$

Since rate is directly proportional to $[\text{H}^+]$ and the protonated form of 1:1 intermediate must be involved in the rate determination step. This corresponds to the intercept in the plot of $k_1/[\text{NO}_2^-]$ vs. $[\text{NO}_2^-]$. The second rate determining stage must be similar to that proposed by Durham *et.al*²⁰ except that the protonated form of this only must be involved in the rate determining step as required by the direct proportionality between k_1 and $[\text{H}^+]$, where as in the reaction with aqueous Cr (VI) reported by Durham *et. al*²⁰, $[\text{H}^+]$ independent path is also present. The Pseudo first order rate constant under the conditions $[\text{NO}_2^-]_i \gg [\text{QDC}]$ did not register any variation with change in total QDC concentration ruling out the possibility of dimeric form of QDC is present in appreciable concentration. The authors therefore consider that the monomeric form of QDC. *i.e.*, QMC is the active oxidizing species. Quinoline added to the reaction mixture of the QDC and the substrate has no effect on the rates of the reaction and this rules out the presence of the pre equilibrium before the rate determining step in the mechanism, and the oxidant reacts only in the form of HQMC, $\text{QH}^+\text{HCrO}_4^-$ after protonation.

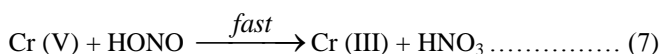
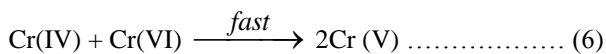


Mechanism

The nitrite ion is almost completely protonated and exists in the form HNO_2 or HONO ($\text{pK}_a=3.398$). Hence the complete mechanism for the entire reaction can be written as



The authors assumed that the intermediate 1:2 complex between HQMC⁺ and nitrous acid (I₂) has the same structure as represented by Durham *et al*²⁰ given for the reaction intermediate.



Applying equilibrium technique leads to the following rate law.

$$\text{Rate} = k_1 [\text{I}_1] + k_2 [\text{I}_2]$$

Under the condition $[\text{NO}_3^-]_t \gg [\text{QHCrO}_4^-]$

$$\text{rate} = \frac{k_1 K_1 K_2 [\text{HONO}] [\text{QHCrO}_4^-] [\text{H}^+] + k_2 K_1 K_2 K_3 [\text{HONO}]^2 [\text{QHCrO}_4^-] [\text{H}^+]}{1 + K_1 [\text{HONO}] + K_1 K_2 [\text{HONO}]^2} \quad \text{----- (8)}$$

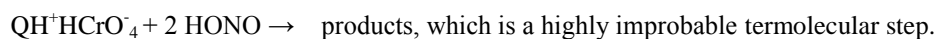
If the magnitudes of K₁ and K₂ are such that both the terms in the denominator can be neglected in comparison with 1, the rate law assumes the form

$$\text{Rate} = k_1 K_1 K_2 [\text{HONO}] [\text{QHCrO}_4^-] [\text{H}^+] + k_2 K_1 K_2 K_3 [\text{HONO}]^2 [\text{QHCrO}_4^-] [\text{H}^+] \quad \text{----- (9)}$$

The pseudo first order rate constant,

$$k_1^1 = k_1 K_1 K_2 [\text{HONO}] [\text{H}^+] + k_2 K_1 K_2 K_3 [\text{HONO}]^2 [\text{H}^+] \quad \text{----- (10)}$$

which agrees with the experimentally determined empirical rate law obtained from the dependence of rate on nitrite ion concentration. The assumption of 1:1 and 1:2 ester type intermediates involving QH⁺HCrO₄⁻ and HNO₂ find justification on theoretical grounds also. If such intermediates are not formed, the second term in the rate law has to be explained in terms of the step.



V. CONCLUSION

The kinetic data and the products obtained in the present investigation demonstrated that the mechanistic path way for the oxidation of nitrite by QDC proceeds by the attack of protonated monomeric QDC i.e., $\{Q H^+ H_2CrO_4\}$ is the active species in the rate determining step.

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