Mechanism of oxidation of hexamine by quinoliniumdichromate (QDC) in aqueous perchloric acid

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The kinetics of oxidation of hexamine by quinoliniumdichromate (QDC) has been investigated spectrophotometrically in aqueous perchloric acid medium at constant ionic strength. The reaction is first order with respect to oxidant and reductant. Increase in perchloric acid concentration increases the reaction rate and order with respect to acid concentration is nearly two. The added products chromium(III), formaldehyde and oxime do not have any significant effect on the rate of reaction. Increase in ionic strength and decrease in dielectric constant of the reaction medium increases the rate of reaction. A suitable mechanism is proposed and the constants involved have been obtained. The activation parameters were evaluated with respect to slow step of the mechanism and discussed.

Keywords: Oxidation, Reduction, Kinetics, Hexamine, Quinoliniumdichromate(QDC)
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Hexamine($C_6H_{12}N_4$) also known as hexamethylene-tetramine, methenamine and urotropine, is simple and convenient source of anhydrous formaldehyde for use in chemical industry. It is the raw material for high explosive like RDX. Hexamine is used in the manufacture and curing of phenolic resins, as a rubber vulcanization accelerator, as fuel tablets for camping stoves, as absorber of poisonous gases, as a reagent for the detection of gold, mercury, antimony, bismuth and silver. It is also used as a urinary antiseptic. The kinetics and mechanism of oxidation of chromium(VI) has been well studied, chromic acid being one of the most versatile oxidizing agents, reacting with diverse substrates. The development of newer chromium(VI) reagents[1-6] for the oxidation of organic substrates continues to be of interest. The reagent employed in these investigations, quinoliniumdichromate (QDC) $[(C_9H_7NH^+)_2Cr_2O_7^{2-}]$ is a useful versatile oxidant that deserves further investigation. In literature, some kinetic studies of the oxidation of inorganic substrates by QDC are available[7]. Since chromium exhibits different oxidation states during oxidation, such as chromium(V), chromium(IV), chromium(III), etc., the reaction might involve several complexities. There are no reports on the oxidation of hexamine by QDC. Hence, the oxidation of hexamine by QDC in perchloric acid medium has been undertaken to understand the behavior of oxidant and reductant in such medium and to arrive at a suitable mechanism.

Experimental Procedure

Materials

Reagent grade chemicals and double distilled water were used throughout this work. Quinolinium-dichromate(QDC) was prepared by the known method[6] as follows: a known quantity of quinoline was slowly added to a cooled solution of chromium trioxide in water with stirring. After 30 min, the solution was diluted with acetone and cooled to −20°C for about 15 h. The orange solid, which separated out, was filtered, washed with acetone, dried in vacuum and then recrystallised from water. It was charecterised by IR, NMR and from its melting point (159°C, reported 160-161°C). The stock solution of QDC was prepared by dissolving it in water and its concentration was ascertained by iodometrically[6]. A stock solution of hexamine was prepared by dissolving hexamine in water. The chromium(III) solution was prepared by dissolving $Cr_2(SO_4)_3.K_2SO_4.24H_2O$ (BDH, AR) in water. Perchloric acid (70% E. Merck) was the source of H^+, utilized to vary the acid concentration in the reaction media. The ionic strength was maintained with sodium perchlorate (Koch-light).

Kinetic studies

Kinetics were followed at 25.0±0.1°C and at I = 1.10 mol dm^{-3}. The reaction was initiated by mixing previously thermostatted reactant solutions of

quinoliniumdichromate(QDC) and hexamine, which also contained the required quantities of perchloric acid and sodium perchlorate. The kinetics were followed under pseudo-first order conditions with [hexamine] : [QDC] $\geq$ 10 : 1 at constant ionic strength of 1.10 mol dm^{-3}. Progress of the reaction was followed by measuring the absorbance of QDC in the reaction mixture at 440 nm in a 1 cm cell placed in the cell compartment of an Hitachi 150-20 spectrophotometer (Tokyo, Japan). Application of Beer's law under the reaction condition had been verified between 1.0×10^{-4} and 2.0×10^{-3} mol dm^{-3} of QDC at 440 nm with extinction coefficient ε =400±10 dm^3 mol^{-1} cm^{-1}. The pseudo-first order rate constants, k_{obs} were obtained from the slopes of the plot log[a/(a−x)] versus time, where 'a' is the initial concentration of QDC and (a-x) is the decrease in concentration of QDC at different time intervals. The first order plots were linear over 80% completion of the reaction (Fig. 1). The second order rate constants, k_2 were obtained by the ratio of first order rate constant to substrate concentration (Table 1). Duplicate runs agreed within ±5%.

Results and Discussion

Stoichiometry and product analysis

Different sets of reactant concentrations were mixed at constant acidity and ionic strength at 25°C. After 8 h the QDC content was analysed by measuring its absorbance at 440 nm. The concentration of chromium(III) was determined by
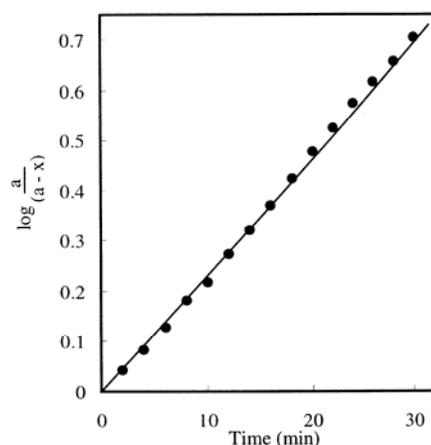

Fig. 1 — Plot of log[a/(a−x)] versus time; [QDC] = 8.0×10^{-4}; [hexamine] = 1.0×10^{-2}; [HClO$_4$] = 1.0; I = 1.10 / mol dm^{-3}

Table 1 — Effect of variation of QDC, hexamine and perchloric acid concentrations on the oxidation of hexamine by QDC at 25°C, and I = 1.10 mol dm^{-3}

[QDC]×10^4 (mol dm^{-3})	[Hexamine]×10^2 (mol dm^{-3})	[HClO$_4$] (mol dm^{-3})	k_{obs}×10^3 (s^{-1})	$k_2 = \dfrac{k_{obs}}{[\text{Hexamine}]}$ (dm^3 mol^{-1} s^{-1})
2.0	1.0	1.0	0.89	-
6.0	1.0	1.0	0.88	-
8.0	1.0	1.0	0.89	-
12.0	1.0	1.0	0.87	-
16.0	1.0	1.0	0.89	-
20.0	1.0	1.0	0.89	-
8.0	0.5	1.0	0.44	0.088
8.0	1.0	1.0	0.89	0.089
8.0	2.0	1.0	1.78	0.089
8.0	3.0	1.0	2.64	0.088
8.0	4.0	1.0	3.50	0.088
8.0	5.0	1.0	4.47	0.089
8.0	1.0	0.25*	0.17	-
8.0	1.0	0.50	0.58	-
8.0	1.0	1.00	2.24	-
8.0	1.0	1.50	5.48	-
8.0	1.0	2.00	8.71	-
8.0	1.0	2.50	13.2	-

*In the case of variation of acid concentration the ionic strength was kept constant at I = 2.60 mol dm^{-3}

measuring the absorbance at 580 nm. Other reaction products were identified as formaldehyde and oxime by their spot tests[8]. The oxime was confirmed by its IR spectrum which showed the band at 1628 cm^{-1} for

C = N – and – OH stretching at 3419 cm^{-1}. A test for formic acid was negative. The results indicate that two moles of quinoliniumdichromate reacts with three moles of hexamine as given in Eq. (1).

$$\cdots(1)$$
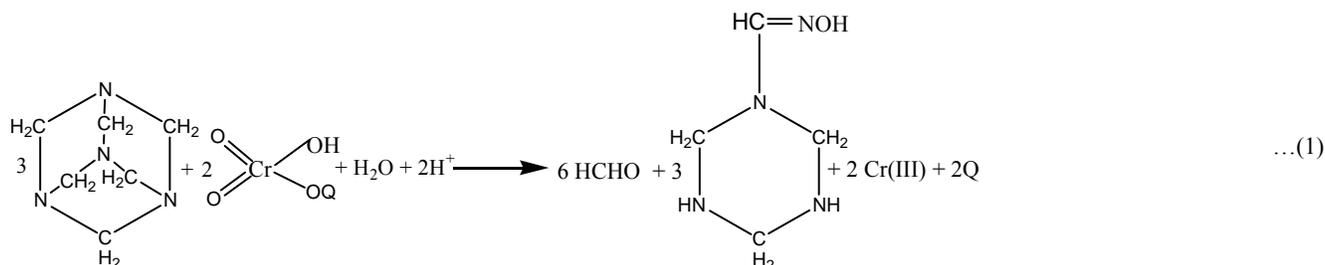
Reaction order

The reaction order was determined from the plots of log k_{obs} versus log(concentration). The order with respect to QDC in the 2.0×10^{-4}-2.0×10^{-3} mol dm^{-3} concentration range was found to be unity, at constant reductant, [hexamine] $=1.0\times10^{-2}$ mol dm^{-3}, acid, [HClO$_4$] $=1.0$ mol dm^{-3} and at constant ionic strength I = 1.10 mol dm^{-3}. The pseudo-first order rate constants, k$_{obs}$ were constant for different initial QDC concentrations (Table 1) and log[a/(a−x)] versus time plots were also linear over 80% completion of the reaction confirming the unit order in QDC concentrations. The order with respect to hexamine concentration was determined by varying the hexamine (Table 1) in the concentration range 5.0×10^{-3} and 5.0×10^{-2} mol dm^{-3} at fixed concentrations of oxidant, acid and at constant ionic strength, the order with respect to hexamine concentration was also found to be unity.

Effect of acid

At constant concentration of oxidant, reductant and at constant ionic strength, as the perchloric acid concentration increases the rate of the reaction increases (Table 1). The order with respect to acid concentration, from a plot of k_{obs} versus log[HClO$_4$], was found to be nearly two (*ca* 1.92) in the 0.25-2.5 mol dm^{-3} concentration range of perchloric acid. A plot of k_{obs}/[HClO$_4$] versus [HClO$_4$] is linear (Fig. 2) with a very small intercept, the slope being nearly 10 times greater than the intercept. Thus, the reaction involving two protons, either as the monoprotonated oxidant species or diprotonated oxidant species is likely to be the dominant path.

Effect of added products

The effects of initially added products, chromium(III), formaldehyde and oxime were studied
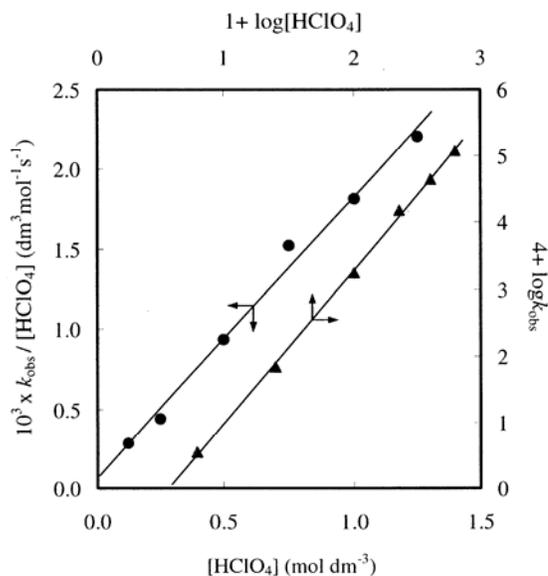

Fig. 2 — Order with respect to HClO$_4$ concentration and the plot of k_{obs}/[HClO$_4$] versus [HClO$_4$] (conditions as in Table 1)

in the concentration range 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3} by keeping the reactant concentrations and all other conditions constant. None of the added products had any significant effect on the rate of reaction.

Effect of dielectric constant and ionic strength

When the acetic acid content (*v/v*) in the reaction medium was increased i.e. when the dielectric constant (D) of the medium decreased, keeping the reactants and other conditions constant, the pseudo-first order rate increased. Since the dielectric constants of aqueous acetic acid are not available in the literature, they were computed from the values of pure liquids[9]. No appreciable reaction of the solvent with the oxidant occurred under the experimental conditions employed. A logk_{obs} versus 1/D plot was linear with positive slope (Fig. 3). Variation of ionic strength between 1.10 and 3.50 mol dm^{-3} using

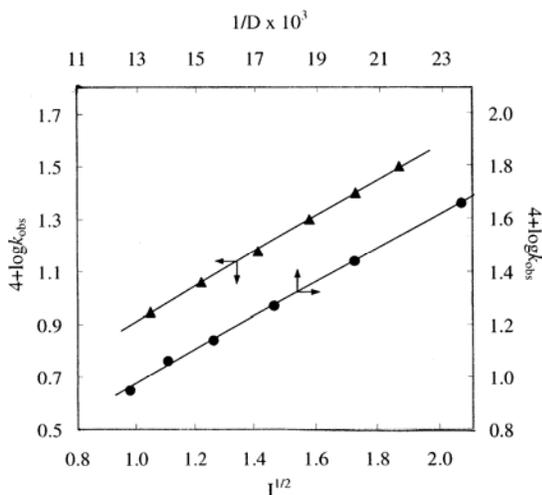Fig. 3 — Plot of $\log k_{obs}$ versus $1/D$ and $\log k_{obs}$ versus $I^{1/2}$
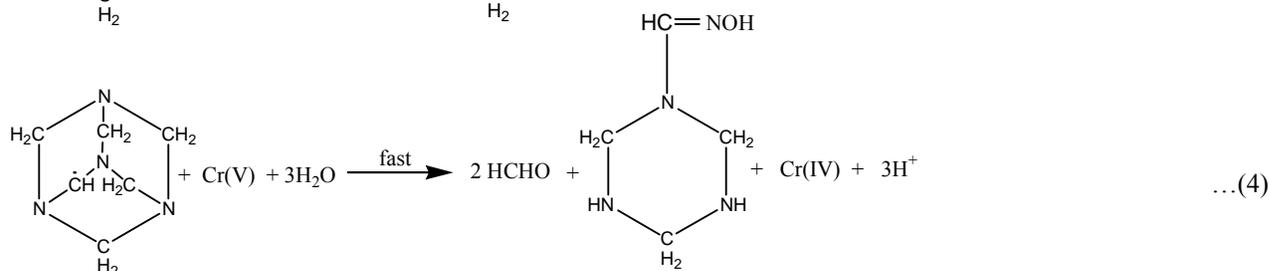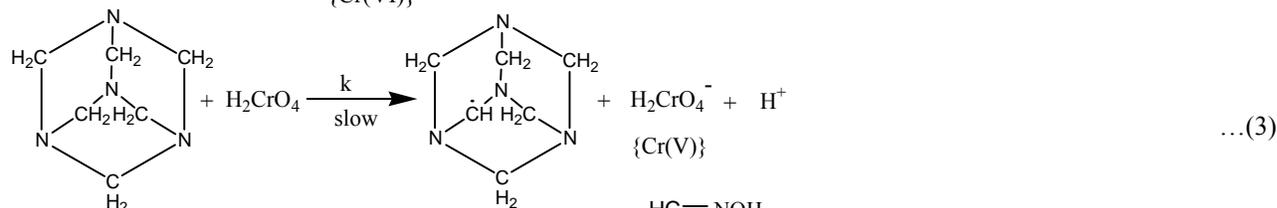
Table 2 — (a) Effect of variation of temperature on the oxidation of hexamine by quinoliniumdichromate in aqueous perchloric acid medium with respect to slow step of Scheme 1

$[QDC] = 8.0 \times 10^{-4}$; $[hexamine] = 1.0 \times 10^{-2}$; $I = 1.10/mol\ dm^{-3}$

Temperature (K)	k (dm^3 mol^{-1} s^{-1})
293	0.50
298	0.80
303	1.33
308	2.00

(b) Activation parameters with respect to slow step.

Parameters	Values
E_a	70 ± 3 kJmol^{-1}
$\Delta H^{\neq}$	68 ± 3 kJmol^{-1}
$\Delta S^{\neq}$	-20 ± 1 J K^{-1}mol^{-1}
$\Delta G^{\neq}$	74 ± 3 kJmol^{-1}
logA	12 ± 0.50

sodium perchlorate caused an increase in the rate of the reaction. A plot of $\log k_{obs}$ versus $I^{1/2}$ was linear with positive slope as shown in Fig. 3.

Test for free radicals

The interaction of free radicals was examined as follows: The reaction mixture, to which a known quantity of acrylonitrile scavenger has been added initially, was kept for 2 h in an inert atmosphere. Upon diluting the reaction mixture with methanol, a white precipitate resulted suggesting the precipitation of free radicals in the reaction.

Effect of temperature

The rate of reaction was measured at four different temperatures with varying perchloric acid concentration, keeping other conditions constant. The rate was found to increase with increase in temperature. The rate constant k of the slow step of

the reaction was obtained from intercept of $1/k_{obs}$ versus $1/[HClO_4]$ at different temperatures (Table 2). The energy of activation was obtained from the plot of $\log k$ versus $1/T$, from which the activation parameters were calculated and are given in Table 2.

The oxidation of hexamine by quinolinium-dichromate (QDC) in aqueous perchloric acid solutions has a stoichiometry of 2:3 i.e. two moles of quinoliniumdichromate require three moles of hexamine. Variations of the concentrations of each of the oxidant (QDC), substrate (hexamine) and acid (perchloric acid), while keeping all other conditions constant, showed that the reaction exhibits first order with respect to oxidant and substrate concentrations and nearly two (~1.92) order with respect to acid concentration. These experimental results can be accommodated in the form of following mechanism (Scheme 1).

$$QDC + 2H^+ \overset{K}{\rightleftharpoons} H_2CrO_4 + Q\ (Quinoline)$$
$$\{Cr(VI)\}$$

...(2)

...(3)

...(4)
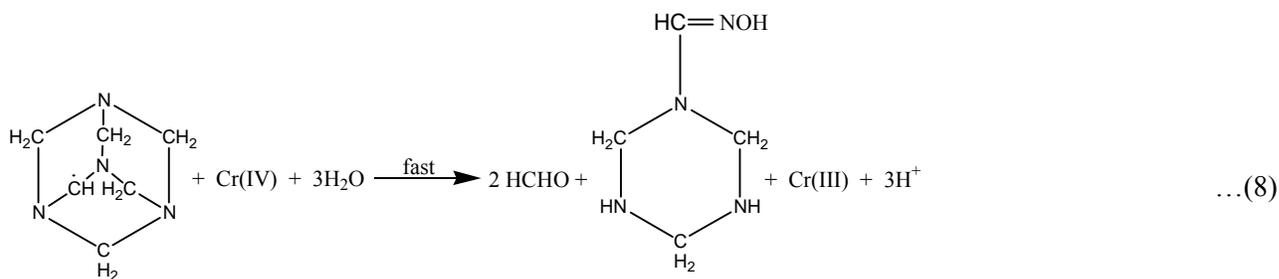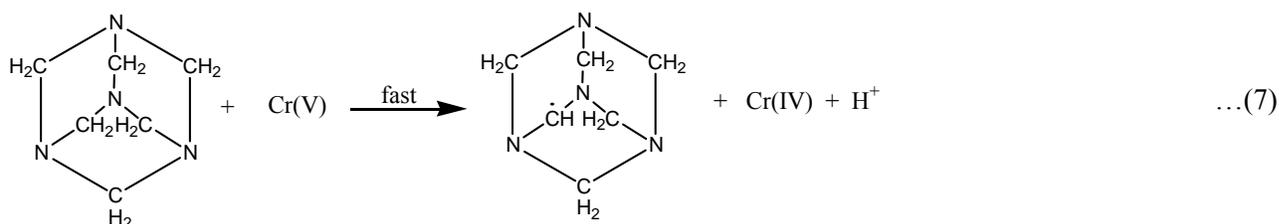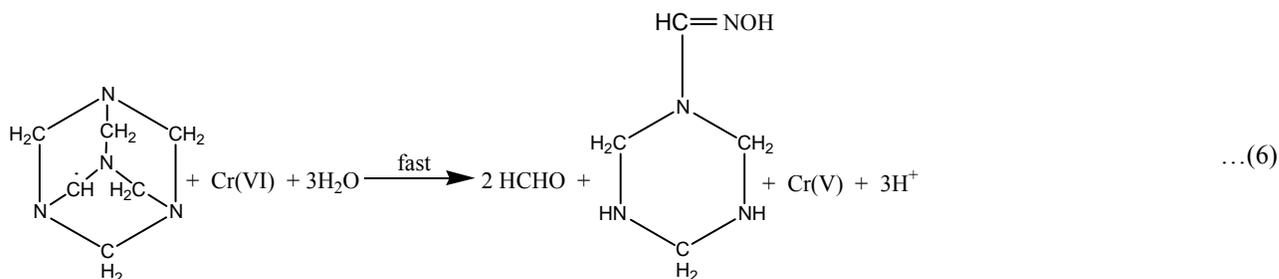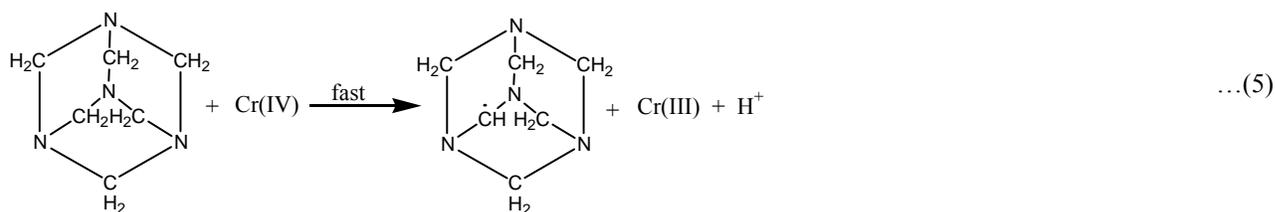
Scheme 1

In a pre-equilibrium step, QDC reacts with two moles of acid to give H_2CrO_4 species which is in accordance with observed order of nearly two in acid concentration. It is a well known fact that in aqueous acid solutions chromium(VI) exists mainly in the form[7,10] of H_2CrO_4. In view of the observed order of unity in both hexamine and QDC concentrations, hexamine reacts with H_2CrO_4 in a rate-determining step to give a free radical derived from hexamine and chromium(V) being generated. This intermediate chromium(V) reacts with the free radical of hexamine in a fast step to give the products, formaldehyde, oxime and the intermediate chromium(IV) species. Another molecule of hexamine reacts with chromium(IV) species in a further fast step to give a free radical derived from hexamine and the product chromium(III) and further followed by other fast steps

to give the products. The initiation of polymerization of acrylonitrile indicated the presence of a free radical intermediate (vide infra). A free radical mechanism has been proposed[11] for the oxidation of 2-propanol by chromium(VI) in aqueous acetic acid medium. The oxidation of hexamine by quinoliniumdichromate occurs by the intervention of reactive chromium(V) and chromium(IV) species. The intervention of chromium(V) is evident from the induction experiment with iodide[12]. The induced oxidation of iodide yields two equivalent of iodine for each equivalent of the inductor oxidized. The induction factor for iodide oxidation is nearly two, which indicates that the active oxidizing agent is pentavalent chromium. The intervention of chromium(IV) is evident from the progressive rate decrease in the presence of increasing amounts of added

manganese(II), the decrease reaching a limit of about one half of the rate found in the absence of manganese(II). Such results have also been obtained for chromium(VI) oxidation of 2-propanol in acetic acid[11].

From Scheme 1, the rate law (11) may be obtained as follows:

$$\text{Rate} = \frac{d[\text{QDC}]}{dt} = k[\text{hexamine}][\text{H}_2\text{CrO}_4]$$

But, from first step of Scheme 1 one has

$$[\text{H}_2\text{CrO}_4] = K[\text{QDC}][\text{H}^+]^2$$

Therefore,

$$\text{Rate} = kK\,[\text{hexamine}][\text{QDC}][\text{H}^+]^2 \qquad \ldots(9)$$

The total concentration of quinoliniumdichromate, $[\text{QDC}]_t$ is given by

$$[\text{QDC}]_t = [\text{QDC}]_f + \text{H}_2\text{CrO}_4$$

$$= [\text{QDC}]_f + K[\text{QDC}][\text{H}^+]^2$$

$$= [\text{QDC}]_f\,\{1 + K[\text{H}^+]^2\}$$

Therefore,

$$[\text{QDC}]_f = \frac{[\text{QDC}]_t}{\{1 + K[\text{H}^+]^2\}} \qquad \ldots(10)$$

where 't' and 'f' stand for total and free. Substituting Eq. (10) in Eq. (9) and omitting the subscripts one gets

$$\text{Rate} = \frac{kK[\text{QDC}][\text{hexamine}][\text{H}^+]^2}{1 + K[\text{H}^+]^2}$$

or

$$\frac{\text{Rate}}{[\text{QDC}]} = k_{\text{obs}} = \frac{kK[\text{QDC}][\text{hexamine}][\text{H}^+]^2}{1 + K[\text{H}^+]^2} \qquad \ldots(11)$$

The rate law (11) explains all the experimentally observed orders and it is rearranged to Eq. (12), which is suitable for verification.

$$\frac{[\text{hexame}]}{k_{\text{obs}}} = \frac{1}{kK[\text{H}^+]^2} + \frac{1}{k} \qquad \ldots(12)$$
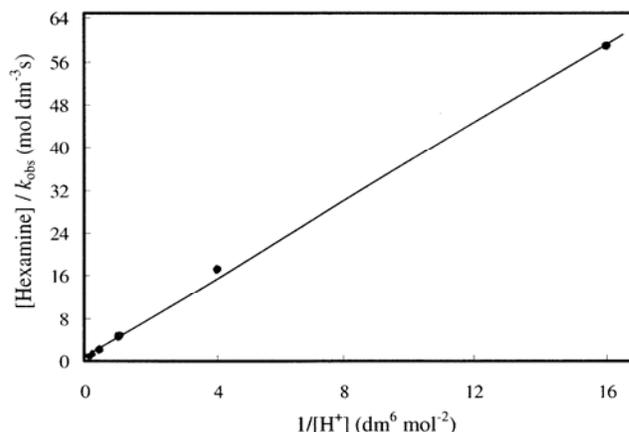

Fig. 4 — Verification of rate law (11) in the form of (12)
(conditions as in Table 1)

According to Eq. (12), the plot of LHS versus $1/[\text{H}^+]^2$ should be linear and is found to so (Fig. 4). The intercept and slope of the plot lead to the values of k and K as (0.8 ± 0.02) dm^{3}mol^{-1} s^{-1} and (0.35 ± 0.02) dm^6 mol^{-2}, respectively.

The effect of ionic strength is difficult to interpret in view of the various ions involved in the reaction and high ionic strength used. The effect of solvent on the reaction rate has been described in detail in the literature[13]. An increase in the content of acetic acid in the reaction medium leads to increase in the reaction rate. The plots of $\log k_{\text{obs}}$ versus $1/D$ was linear with positive slope which is contrary to the expected. Perhaps the effect is countered substantially by the formation of active reaction species to a greater extent in low dielectric constant media leading to the net increase in the rate[14]. The mechanism is also supported by moderate values of thermodynamic parameters. The value of $\Delta S^{\neq}$ within the range of radical reactions has been ascribed to the nature of electron pairing and electron unpairing processes and to the loss of degree of freedom formerly available to the reactions[15].

Conclusion

The main products of the reaction were found to be chromium(III), formaldehyde and oxime. A mechanism in terms of active species of oxidant and reductant is proposed and the rate law is derived and verified.

Acknowledgement

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