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Kinetic and Mechanistic Studies in the Oxidative Regeneration of Carbonyl Compounds from Oximes by Quinolinium Chlorochromate

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ABSTRACT

The oxidative deoxidization of several aldol- and keto-oximes by quinolinium chlorochromate (QCC), in dimethylsulphoxide (DMSO), exhibited a first order dependence on QCC. Michaelis-Menten type kinetics was observed with respect to oximes. The oxidation of ketoximes is slower than that of aldoximes. The rates of oxidation of aldoximes correlated well in terms of Pavelich-Taft dual substituent-parameter equation. The low positive value of polar reaction constant indicated a nucleophilic attack by a chromate-oxygen on the carbon. The reaction is subject to steric hindrance by the alkyl groups. The reaction of acetaldoxime has been studied in nineteen different organic solvents. The solvent effect has been analysed by multiparametric equations. A mechanism involving the formation of a cyclic intermediate, in the rate-determining step is suggested.

Keywords: Carbonyl compounds, Dichromates, Kinetics, Mechanism, Oxidation, Oximes.

INTRODUCTION

Regeneration of carbonyl compounds from its derivatives under mild conditions is an important process in synthetic organic chemistry. Several oxidative methods are available for deoximation [1] Salts of Cr (VI) have long been used as oxidizing reagents in synthetic organic chemistry. However, these salts are drastic and non-selective oxidants in nature. Further, they are insoluble in most of the organic solvents also. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr (VI) have been prepared and used in synthetic organic syntheses as mild and selective oxidants in non-aqueous solvents [2]. One such compound is quinolinium chlorochromate (QCC) [3]. Only a few reports are available in literature regarding oxidation aspects of QCC [4-6]. It is known that the mode of oxidation depends on the nature of the counter-ion attached to the chromium anion. Therefore, in continuation of our earlier work [7-11], we report here the kinetics of the oxidative deoximation of several aldo- and keto-oximes by QCC in several organic solvents but mainly in dimethylsulphoxide (DMSO). Mechanistic aspects have also been discussed.

MATERIALS AND METHODS

Materials: Oximes were prepared by the reported standard methods [12] and their mp was checked with the literature values. QCC also was prepared by the reported method[3]. Solvents were purified by the usual procedure [13]

Product Analysis: The oxidation of the oximes results in the regeneration of corresponding carbonyl compounds, as confirmed by TLC (eluent: CCl_4/Et_2O). Isolation of the product was attempted in the oxidation of oximes of benzaldehyde and acetophenone. In a typical experiment, the oxime (0.2 mol) and QCC (0.02 mol) were dissolved in 50 mL of DMSO and allowed to stand for *ca*. 10 h for the completion of the reaction. Silica gel (5 g) was then added to the reaction mixture and the mixture was stirred for 15 min [14]. It was then filtered and the solid residue was washed with the solvent (2 % 15 mL). The solvent was removed on a rotary evaporator and the residue was purified on a silica-gel column (eluent: CCl_4/Et_2O). Evaporation of the solvent afforded the pure carbonyl compound. Yields of benzaldehyde and acetophenone were 1.83 g (86%) and 2.11 g (88%) respectively. The presence of HNO_2 in completely reduced reaction mixtures was confirmed by a positive starch-iodide test [15]. The oxidation state of chromium in a completely reduced reaction mixture, as determined by an iodometric method, is 3.95±0.10.

Kinetics Measurements: The reactions were studied under pseudo-first-order conditions by keeping a large excess (× 10 or greater) of the oxime over QCC. The solvent was DMSO, unless mentioned otherwise. The reactions were studied at constant temperature (±0.1 K). The reactions were followed by monitoring the decrease in the concentration of QCC at 352 nm spectrophotometrically. The pseudo-first-order rate constant, k_{obs}, was evaluated from the linear least-squares plots of log [QCC] *versus* time. Duplicate kinetic runs showed the rate constants to be reproducible to within ±4%. The second order rate constants were evaluated from the relation $k_2 = k_{obs}/[\text{reductant}]$.

RESULTS AND DISCUSSION

Stoichiometry: The analysis of products indicated the following overall reaction.

$$R_2C = N\text{–}OH + 2\,CrO_2ClOQH \longrightarrow R_2C = O + HNO_2 + 2\,CrOClOQH \quad \dots (1)$$

QCC undergoes two-electron change. This is in accordance with the earlier observations with structurally similar other halochromates also. It has already been shown that both PFC [16] and PCC [17] act as two electron oxidants and are reduced to chromium (IV) species by determining the oxidation state of chromium by magnetic susceptibility, ESR and IR studies.

Rate Laws: The reactions are of first order with respect to QCC. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of QCC. The reaction rate increases with increase in the concentration of the oximes but not linearly (Table 1). The figure 1 depicts a typical kinetic run. A plot of $1/k_{obs}$ against 1/[Oxime] is linear (r > 0.995) with an intercept on the rate-ordinate. Thus, Michaelis-Menten type kinetics is observed with respect to oximes. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

$$\text{Oxime} + \text{QCC} \overset{K}{\leftrightarrows} [\text{Complex}] \quad \dots(2)$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Products} \quad \dots(3)$$

$$\text{Rate} = k_2 K [\text{Oxime}] [\text{QCC}] / (1 + K [\text{Oxime}]) \quad \dots(4)$$

The dependence of k_{obs} on the concentration of oxime was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic parameters for the complex formation and activation parameters of the disproportionation of the complexes, at 298 K, were calculated from the values of K and k_2 respectively at different temperatures (Tables 2 and 3, fig 2).

Table 1: Rate constants for the oxidation of acetaldoxime by QCC at 288 K

10^3 [QCC] / mol dm^{-3}	[Oxime] / mol dm^{-3}	10^4 k_{obs} / s^{-1}
1.00	0.10	9.30
1.00	0.20	13.6
1.00	0.40	17.6
1.00	0.60	19.6
1.00	0.80	20.8
1.00	1.00	21.5
1.00	1.50	22.6
1.00	3.00	23.8
2.00	0.20	13.5
4.00	0.20	12.6
6.00	0.20	14.4
8.00	0.20	13.9

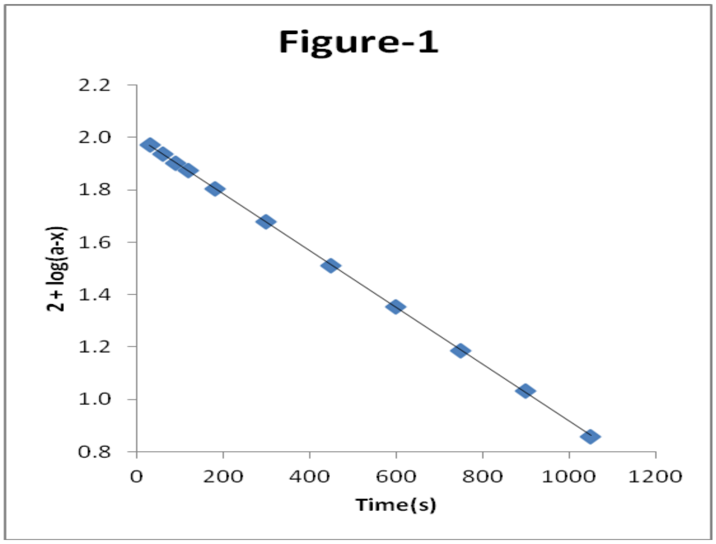


Figure 1. Oxidation of Acetaldoxime by QCC: A typical Kinetic Run

Table 2: Rate constants and activation parameters for the oxidation of QCC-Oximes (R^1 R^2 C = N – OH) Complexes

Subst (R)	10^4 k_2 / (dm^3 mol^{-1} s^{-1})				ΔH^*	$-\Delta S^*$	ΔG^*
	288	298	308	318	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJ mol^{-1})
H – H	1240	1380	1490	1570	34.9±0.3	250±1	78.0±0.3
H – Me	25.2	40.5	62.1	93.6	30.7±0.1	188±1	86.7±0.1
H – Et	18.0	29.7	47.7	73.8	33.3±0.1	182±1	87.4±0.1
H – Pr	8.55	15.3	25.2	42.3	37.8±0.3	173±1	89.1±0.3
H – Pr^i	5.76	10.8	18.0	32.4	40.8±0.7	166±2	90.0±0.6
H – $ClCH_2$	79.2	108	135	171	16.8±0.5	227±2	84.3±0.4
H – Ph	52.2	77.4	108	153	24.6±0.3	204±1	85.1±0.2

Me – Me	2.61	4.14	6.39	9.81	31.0±0.2	206±1	92.3±0.2
Me – Et	2.07	3.24	5.04	7.83	31.2±0.4	207±1	92.9±0.3
Et – Et	1.71	2.70	4.23	6.66	31.9±0.5	207±2	93.3±0.4
Me – Ph	4.59	7.83	13.5	22.5	37.9±0.4	178±1	90.7±0.3

Table 3: Formation constants and thermodynamic parameters of the oxidation of QCC- Oximes ($R^1 R^2 C = N – OH$) Complexes

Substituent (R)	K / (dm^3 mol^{-1})				$–\Delta H^*$	$–\Delta S^*$	$–\Delta G^*$
	288	298	308	318	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJ mol^{-1})
H – H	6.36	5.52	4.72	3.96	14.5±0.4	27±1	6.70±0.3
H – Me	5.85	5.02	4.25	3.42	16.0±0.7	32±2	6.45±0.6
H – Et	6.45	5.62	4.86	4.02	14.4±0.6	26±1	6.74±0.5
H – Pr	5.94	5.15	4.32	3.53	15.7±0.6	31±2	6.50±0.5
H – Pr^i	5.77	4.95	4.14	3.33	16.4±0.7	34±2	6.41±0.6
H – $ClCH_2$	5.58	4.75	3.93	3.15	17.0±0.7	36±2	6.31±0.5
H – Ph	6.57	5.76	4.92	4.16	14.1±0.4	25±1	6.79±0.4
Me – Me	6.21	5.42	4.56	3.78	15.1±0.6	29±2	6.63±0.5
Me – Et	6.03	5.25	4.43	3.62	15.4±0.7	30±2	6.55±0.5
Et – Et	5.67	4.85	4.07	3.24	16.6±0.7	35±2	6.36±0.6
Me – Ph	5.43	4.60	3.82	3.05	17.0±0.7	37±2	6.23±0.5

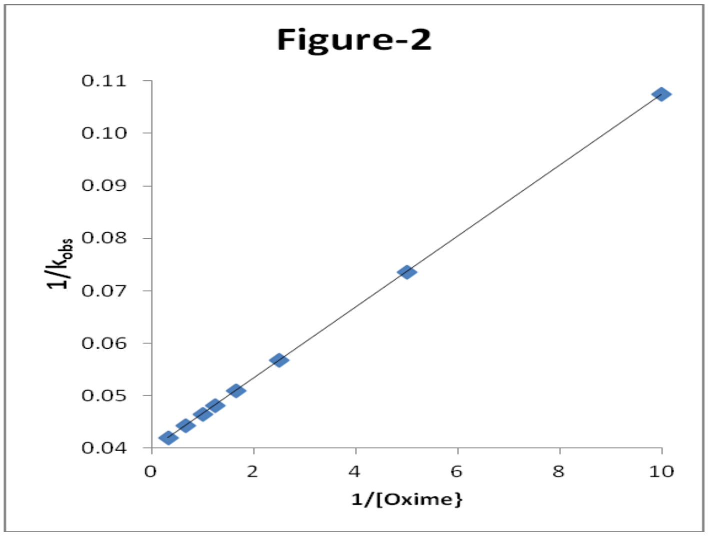


Figure 2 Oxidation of Acetaldoxime by QCC: A double reciprocal plot

Effect of Solvents: The oxidation of acetaldoxime was studied in nineteen different solvents. The choice of solvents was limited due to the solubility of the reactants and the reaction of QCC with primary and secondary alcohols. There was no reaction with chosen solvents. The kinetics was similar in all the solvents. The values of k_2 are recorded in table 4.

Table 4: Effect of solvents on the oxidation of acetaldoxime by QCC at 298 K

Solvents	K (dm^{-3} mol^{-1})	k_{obs} (s^{-1})	Solvents	K (dm^{-3} mol^{-1})	k_{obs} (s^{-1})
Chloroform	4.41	18.2	Toluene	5.31	5.25
1,2-Dichloroethane	5.35	19.9	Acetophenone	5.22	27.5
Dichloromethane	5.19	23.9	THF	5.76	11.2
DMSO	4.25	62.1	t-Butylalcohol	4.70	7.94
Acetone	4.67	20.9	1,4-Dioxane	5.61	9.33
DMF	5.13	31.6	1,2-Dimethoxyethane	4.88	6.17
Butanone	5.99	14.8	CS_2	5.66	3.39
Nitrobenzene	4.89	22.4	Acetic Acid	4.95	4.17
Benzene	5.40	6.46	Ethyl Acetate	5.85	8.51
Cyclohexane	5.38	0.72			

There is no significant isokinetic relationship between activation entropy and enthalpy of the oxidation of oximes (r^2 = 0.2373). A correlation between the calculated values of enthalpies and entropies of activation is often vitiated by the experimental errors associated with them. Exner [18] has suggested an alternative method of testing the validity of the isokinetic relationship. An Exner's plot between log k_2 at 288 and 318 K was linear (r^2 = 0.9958; slope = 0.7145±0.0232; Figure – 3). The value of isokinetic temperature evaluated from this plot is 431±17 K. The linear isokinetic correlation suggests that all the oximes are oxidized by the same mechanism and are governed by the changes in both the enthalpy and entropy of the activation.

Solvent Effect: The rate constants, k_2, of the oxidation of acetaldoxime in eighteen solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (Eq.5) of Kamlet et al. [19].

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \qquad \dots (5)$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for α.

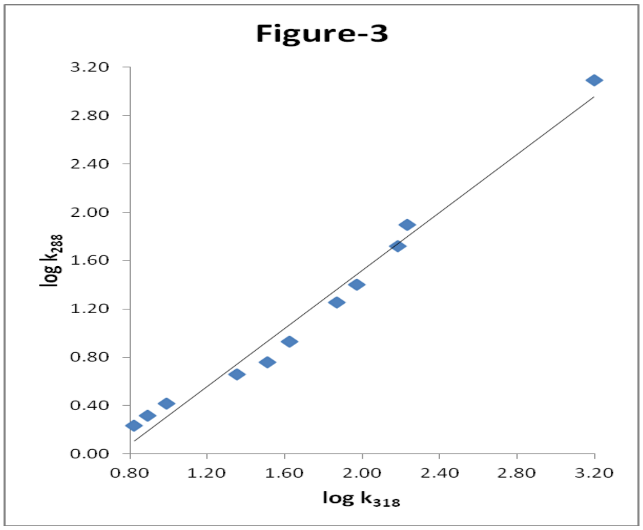


Figure 3: Exner's Isokinetic Relationship in the oxidation of Oximes by QCC

The results of correlation analyses in terms of Eq. (5), a biparametric equation involving π^* and β, and separately with π^* and β are given below [Eqs. (6) - (9)].

$$\log k_2 = -3.97 + 1.58 (\pm 0.19) \pi^* + 0.20 (\pm 0.16) \beta + 0.10 (\pm 0.15) \alpha \quad \ldots (6)$$
$$R^2 = 0.8585; \quad sd = 0.18; \quad n = 18; \quad \psi = 0.41$$
$$\log k_2 = -3.95 + 1.61 (\pm 0.18) \pi^* + 0.17 (\pm 0.15) \beta \quad \ldots (7)$$
$$R^2 = 0.8545; \quad sd = 0.17; \quad n = 18; \quad \psi = 0.40$$
$$\log k_2 = -3.98 + 1.66 (\pm 0.18) \pi^* \quad \ldots (8)$$
$$r^2 = 0.8417; \quad sd = 0.18; \quad n = 18; \quad \psi = 0.41$$
$$\log k_2 = -3.11 + 0.46 (\pm 0.35) \beta \quad \ldots (9)$$
$$r^2 = 0.0964; \quad sd = 0.42; \quad n = 18; \quad \psi = 0.98$$

Here *n* is the number of data points and ψ is Exner's statistical parameter [20].

Kamlet's [19] triparametric equation explains *ca.* 86% of the effect of solvent on the oxidation. However, by Exner's criterion [20] the correlation is not even satisfactory (cf. Eq. 6). The major contribution is of solvent polarity. It alone accounted for *ca.* 84% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's equation[21] of cation- and anion-solvating concept of the solvents also [Eq. (10)].

$$\log k_2 = aA + bB + C \quad \ldots (10)$$

Here A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. (A + B) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of Eq. (7), separately with A and B and with (A+ B).

$$\log k_2 = 0..67 (\pm 0.05) A + 1.66 (\pm 0.04) B - 3.96 \quad \ldots (11)$$
$$R^2 = 0.9931; \quad sd = 0.04; \quad n = 19; \quad \psi = 0.09$$
$$\log k_2 = 0.44 (\pm 0.55) A - 3.08 \quad \ldots (12)$$
$$r^2 = 0.0363; \quad sd = 0.44; \quad n = 19; \quad \psi = 1.01$$
$$\log k_2 = 1.60 (\pm 0.12) B - 3.99 \quad \ldots (13)$$
$$r^2 = 0.9081; \quad sd = 0.14; \quad n = 19; \quad \psi = 0.32$$
$$\log k_2 = 1.33 \pm 0.13 (A + B) - 3.89 \quad \ldots (14)$$
$$r^2 = 0.8627; \quad sd = 0.14; \quad n = 19; \quad \psi = 0.38$$

The rates of oxidation of acetaldehyde in different solvents showed an excellent correlation in Swain's equation [cf. Eq.(11)] with both the anion- and cation-solvating powers playing almost equal role. However, individually A and B are able to account for only 04% and 90% of the data only. The solvent polarity, represented by (A + B), also exhibited an excellent correlation. In view of the fact that solvent polarity is able to account for *ca.* 86% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of $\log k_2$ against the inverse of the relative permittivity is not very significant ($r^2 = 0.5527$; sd = 0.31; $\psi = 0.72$). The analysis of solvent effect indicated the formation of an activated complex which is more polar than the reactants. The rate is affected by the solvent polarity.

Correlation Analysis of Reactivity: We could not find any report about the mechanism of the reaction between a C=N bond and a halochromate derivative. However, the reaction of alkenes with chromium (VI) has been well studied [22]. Since, olefinic bonds are not usually subject to a nucleophilic attack, it has been suggested that in the alkene-chromate reaction, an organometallic derivative is formed initially [22]. The organometallic derivative then changes to a chromium (IV) diester in the rate-determining step. However, carbon-nitrogen double bonds, being dipolar in nature, can be easily attacked by a nucleophile. The data in table 2 showed that the rate of oxidation of ketoximes is much less as compared to that of the aldoximes. The reason for the slower reaction of ketoximes must be steric. As the central carbon changes from a trigonal to a tetragonal state, the crowding around it increases. This increase in the steric crowding will be more in the case of ketoximes as compared to that in aldoximes. This observation is supported by the correlation analysis of the reactivity of the aldoximes also. The rate of oxidation of the aliphatic oximes did not yield significant correlation separately with Tafts's σ^* and E_S values [Eqs. (15); (16)]. The rates were, therefore, correlated with Pavelich-Taft's [23] dual substituent-parameter Eq. (17).

$$\log k_2 = 1.02 \pm 0.60\, \sigma^* - 2.45 \quad \ldots (15)$$

$r^2 = 0.4211$, sd = 0.65, n = 6, $\psi = 0.86$, Temp. = 298 K

$$\log k_2 = 1.14 \pm 0.23\, E_S - 2.27 \quad \ldots (16)$$

$r^2 = 0.8561$, sd = 0.33, n = 6, $\psi = 0.38$, Temp. = 298 K

$$\log k_2 = \rho^* \sigma^* + \delta E_S + \log k_0 \quad \ldots (17)$$

The rates exhibited excellent correlations in terms of the Pavelich-Taft equation (Table 5); the reaction constants are being positive.

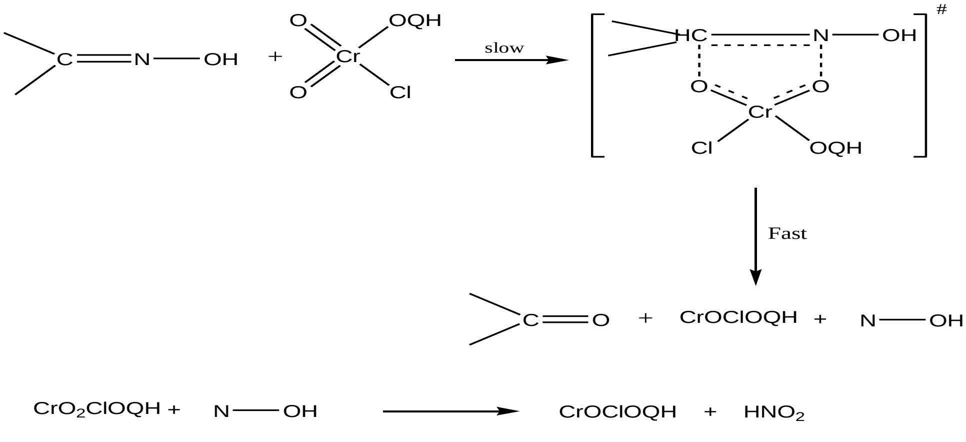
Table 5: Reaction constants for the oxidative deoximination of aliphatic aldoximes by QCC[a]

Temp./K	ρ^*	δ	r^2	Sd	ψ
288	0.72±0.01	1.08±0.01	0.9999	0.001	0.02
298	0.63±0.02	0.98±0.01	0.9998	0.005	0.01
308	0.53±0.01	0.91±0.02	0.9989	0.006	0.01
318	0.43±0.01	0.81±0.01	0.9998	0.003	0.02

[a] Number of compounds is 6

Mechanism: The low positive polar reaction constant points to an almost cyclic transition state in which the formation of the bond between chromate-oxygen and the carbon is somewhat ahead of the formation of N – O bond. This supports a nucleophilic attack by a chromate-oxygen on the carbon. The positive steric reaction constant points to a steric hindrance by the substituents. Therefore, the following mechanism (Scheme 1) is proposed for the reaction. The mechanism is supported by the values of activation parameters also. The low values of enthalpy of activation indicate that the bond-cleavage and bond-formation are almost synchronous. The large negative entropies of activation support the formation of a rigid cyclic activated complex from two acyclic molecules.

The faster oxidation of benzaldoxime may be attributed to the resonance stablization of the cyclic activated complex. The oxidation of benzphenoxime is much slower. This may well be due to steric hindrance by the bulky phenyl and methyl groups. Hydroxynitrene (N-OH) has been recently reported as a very reactive intermediate [24].



Scheme - 1

CONCLUSIONS

Oxidation of oximes by QCC is a reaction subject to the steric hindrance by the alkyl group. Oxidation of ketoximes is slower than acetaldoximes. The reaction proceeds through a cyclic intermediate in the rate-determining step.

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