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Kinetics and Mechanism of the Oxidation of DL-Methionine by Quinolinium Chlorochromate

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ABSTRACT

The oxidation of methionine (Met) by tetrakis (pyridine) silver dichromate (QCC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding sulphoxide. The reaction is first order with respect to QCC. Michaelis-Menten type kinetics was observed with respect to methionine. The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b\,[H^+]$. *The effect of nineteen solvents on oxidation is fitted in Kamlet's and Swain's multiparametric equations. This Study indicates cation-solvating power of the solvent. A suitable mechanism has been postulated.*

Keywords: Halochromate, Kinetics, Kamlet's and Swain's model, Methionine, Oxidation.

INTRODUCTION

Cr(VI) salts of have long been used as oxidizing reagents in synthetic organic chemistry. However these salts are rather drastic in nature and non-selective oxidants. Further, they are insoluble in most of the organic solvents. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in organic synthesis as mild and selective oxidants in non-aqueous solvents [1]. One of such compounds is quinolinium chlorochromate (QCC) reported by Firozabadi *et al.*[2]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complex salts of Cr(VI) and several studies have already been reported from our laboratory[3-6]. It is, known however, that mode of oxidation depends upon the nature of counter-ion attached to the chromium anion. Methionine (Met), a sulphur-containing essential amino acid, is reported to behave differently from other amino acids, towards many oxidants [7,8], due to electron-rich sulphur center which is easily oxidizable. There are no reports on the QCC and mechanism. We report here the kinetics and mechanism of oxidation of DL-methionine by QCC in dimethylsulphoxide (DMSO).

MATERIALS AND METHODS

QCC was prepared by the reported method [2] and its purity was assessed by an iodometric method. Methionime (Merck) was used as supplied. Due to non-aqueous nature of the solvent, toluene-*p*-sulphonic acid (TsOH) was used as a source of hydrogen ions. Other solvents were purified by the usual methods [9].

Product Analysis

Product analysis was carried out under kinetic conditions. The oxidation of Met by QCC resulted in the formation of corresponding sulphoxide, which was determined by the reported method [10]. The yield of sulphoxide was 94±3%. The oxidation state of chromium in completely reduced reaction mixtures, as determined iodometrically, was +4.

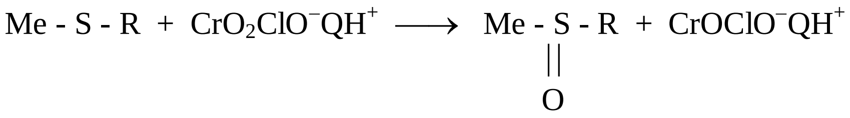
Kinetic measurements

The pseudo-first order conditions were maintained by a large excess (× 15 or more) of the Met over QCC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures (±0.1 K), by monitoring the decrease in [QCC] spectrophotometrically at 370 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constant, k_{obs}, was calculated from the linear ($r = 0.990 - 0.999$) plots of log [QCC] against time for up to 80% reaction. Duplicate kinetic runs showed that the rate constants were reproducible to with in ±3%. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH. The second order rate constant, $\mathrm{k_2}$, was calculated from the relation $\mathrm{k_2 = k_{obs}/[Met]}$. Simple and multivariate linear regression analyses were carried out by the least squares method on a personal computer.

RESULTS AND DISCUSSION

Stoichiometry

The oxidation of methionine by QCC resulted in the formation of the corresponding sulfoxides. The overall reaction may therefore, be represented as equation (1).



$$\mathrm{Me - S - R\ +\ CrO_2ClO^-QH^+} \longrightarrow \mathrm{Me - \underset{\underset{\displaystyle O}{||}}{S} - R\ +\ CrOClO^-QH^+} \qquad (1)$$

Where R is $\mathrm{CH_2CH_2CH(NH_2)COOH}$

QCC undergoes a two-electron change. This is in according with the earlier observations with structurally similar halochromates. It has already been proved earlier also that both pyridinium fluorochromate (PFC)[11] and pyridinium chlorochromate (PCC)[12] act as two electron oxidants and are reduced to chromium (IV) species.

Rate Laws

The reactions were found to be first order with respect to QCC (Figure 1).

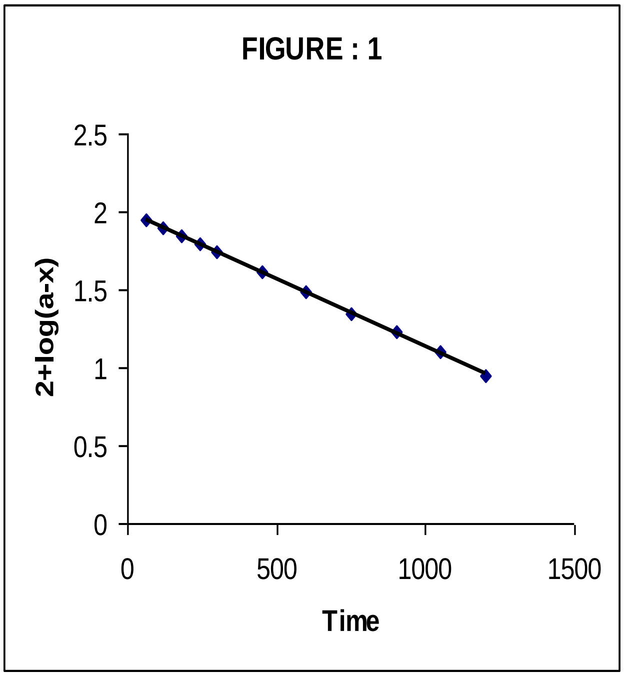


Figure 1 – Oxidation of Methionine by QCC: A typical Kinetic Run

In individual kinetic runs, plots of log [QCC] *versus* time were linear ($r^2 > 0.995$). Further, it was found that the observed rate constant, k_{obs}, does not depend on the initial concentration of QCC. The order with respect to methionine was less than one (Table 1).

Table – 1: Rate constants for the oxidation of methionine by QCC at 298 K

10^3[QCC] mol dm^{-3}	[Met] mol dm^{-3}	10^4k_{obs} s^{-1}
1.0	0.10	6.82
1.0	0.20	10.1
1.0	0.40	13.4
1.0	0.60	15.0
1.0	0.80	15.9
1.0	1.00	16.6
1.0	1.50	17.6
1.0	3.00	18.6
2.0	0.40	14.4
4.0	0.40	12.6
6.0	0.40	14.9
8.0	0.40	13.1
1.0	0.20^*	11.7^*

* contained 0.001 mol dm^{-3} acrylonitrile

A plot of $1/k_{obs}$ *versus* 1/[Met] was linear with an intercept on the rate ordinate (Figure 2).

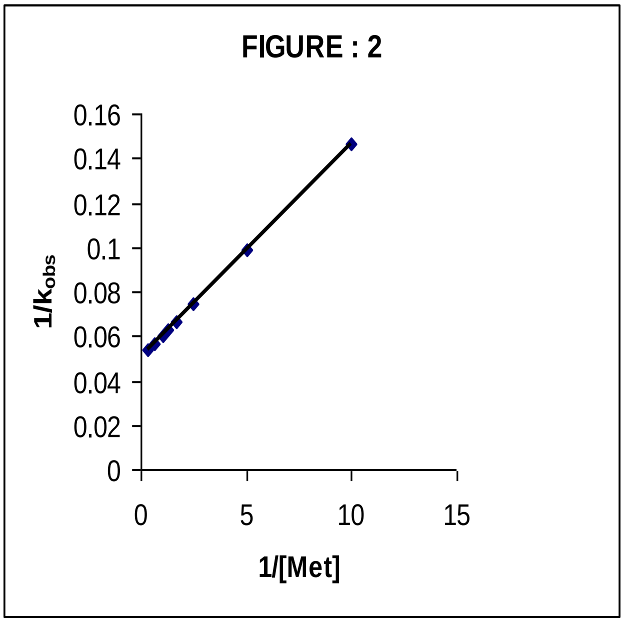


Figure 2 – Oxidation of Methionine by QCC: A double reciprocal plot

The following overall mechanism (equations 2 and 3) and the rate law (4) holds good

$$\text{MeSR} + \text{QCC} \overset{K}{\leftrightarrows} [\text{Complex}] \qquad (2)$$

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

$$\text{Rate} = k_2 K [\text{MeSR}] [\text{QCC}] / (1 + K [\text{MeSR}]) \qquad (4)$$

The dependence of k_{obs} on the concentration of methionine 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 (Tables 3 and 4).

Table – 3: Formation constants and thermodynamic parameters of the oxidation of QCC-Met complexes

K / (dm^3 mol^{-1})				$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J mol^1 K^{-1})	(kJ mol^{-1})

6.03	5.25	4.38	3.60	15.6±0.7	31±2	6.55±0.5

Table – 4: Rate constants and activation parameters of the decomposition of QCC-Met complexes

$10^4\ k_2$ / (dm^3 mol^{-1} s^{-1})				ΔH^*	ΔS^*	ΔG^*
288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J mol^{1} K^{-1})	(kJ mol^{-1})
8.82	19.8	42.3	92.7	57.0±0.6	–106±2	88.4±0.5

Induced Polymerization of Acrylonitrito test for free radicals

The oxidation of Met, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation (Table 1). Therefore, a one-electron oxidation, giving rise to free radicals, is unlikely. To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm^{-3} of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

Effect of acidity

The reaction was studied at different acidities by adding varying amount of toluene-p-sulphonic acid (TsOH) to the reaction mixtures. The reaction is catalyzed by hydrogen ions (Table 2).

Table – 2: Dependence of the reaction rate on hydrogen ion concentration

[Met] 0.10 mol dm^{-3} [QCC] 0.001 mol dm^{-3} Temp. 298 K

[TsOH]/ mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
$10^4\ k_{obs}$/s^{-1}	7.92	9.45	11.7	14.4	17.1	18.9

The hydrogen-ion dependence has the form $k_{obs} = a + b\,[H^+]$. The values of *a* and *b* are 6.86±0.21×10^{-4} s^{-1} and 12.4±0.35×10^{-4} mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9968$).

Solvent Effect

The oxidation of Met was studied in nineteen organic solvents. The choice of solvents was limited due to the solubility of QCC and its reaction with primary and secondary alcohols. There was no reaction with the chosen solvents. The kinetics are similar in the all the solvents. The values of K and k_2 are recorded in Table 5.

Table – 5: Effect of solvents on the oxidation of Methionine by QCC at 298 K

Solvents	K ($dm^3\ mol^{-1}$)	$10^5\ k_2$ (s^{-1})	Solvents	K ($dm^3\ mol^{-1}$)	$10^5\ k_2$ (s^{-1})
Chloroform	6.12	75.9	Toluene	5.64	14.8
1,2-Dichloroethane	4.59	67.6	Acetophenone	5.22	70.8
Dichloromethane	5.98	63.1	THF	5.55	27.5
DMSO	5.25	198	t-butylalcohol	4.86	33.9
Acetone	5.31	52.5	1,4-Dioxane	4.69	30.2
DMF	5.45	93.3	1,2-Dimethoxyethane	4.98	17.0
Butanone	6.03	41.7	CS_2	5.40	7.76
Nitrobenzene	4.95	77.6	Acetic acid	5.44	33.1
Benzene	5.33	19.5	Ethyl acetate	5.63	20.4
Cyclohexane	5.85	1.86			

A perusal of the data shows that the formation constants do not vary much with the nature of the solvents. However, the rate constants, k_2 varied considerably with the solvents. The rate constants for oxidation, k_2, in eighteen solvents (CS_2 was not considered, as the complete range of the solvent parameters was not available) were correlated in terms of the linear solvation energy relationship equation (6) of Kamlet et al [13].

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \qquad (6)$$

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. The results of correlation analyses in terms of equation (6), a biparametric equation involving π^* and β, and separately with π^* and β are given below.

$$\log k_2 = -4.36 + 1.70\ (\pm 0.18)\ \pi^* + 0.13\ (\pm 0.15)\ \beta + 0.31\ (\pm 0.14)\ \alpha \qquad (7)$$
$$R^2 = 0.8792;\quad sd = 0.17;\quad n = 18;\quad \psi = 0.38$$

$$\log k_2 = -4.44 + 1.59\ (\pm 0.19)\ \pi^* + 0.24\ (\pm 0.16)\ \beta \qquad (8)$$
$$R^2 = 0.8392;\quad sd = 0.19;\quad n = 18;\quad \psi = 0.43$$

$$\log k_2 = -4.51 + 1.65\ (\pm 0.20)\ \pi^* \qquad (9)$$
$$r^2 = 0.8158;\quad sd = 0.19;\quad n = 18;\quad \psi = 0.44$$

$$\log k_2 = -2.63 + 0.52\ (\pm 0.35)\ \beta \qquad (10)$$
$$r^2 = 0.1199;\quad sd = 0.42;\quad n = 18;\quad \psi = 0.97$$

Here n is the number of data points and ψ is the Exner's statistical parameter[14].

Kamlet's triparametric equation explains *ca.* 89% of the effect of solvent on the oxidation. However, by Exner's [14] criterion the correlation is not even satisfactory (*cf.* eqn. 7). The major contribution is of solvent polarity. It alone accounted for *ca.* 88% 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 [15] of cation- and anion-solvating concept of the solvents as well.

$$\log k_2 = aA + bB + C \qquad (11)$$

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 equation (11), separately with A and B and with (A + B).

$$\log k_2 = 1.25\,(\pm 0.03)\,A + 1.57\,(\pm 0.02)\,B - 3.84 \qquad (12)$$
$$R^2 = 0.9975;\; sd = 0.02;\; n = 19;\; \psi = 0.05$$

$$\log k_2 = 1.03\,(\pm 0.52)\,A - 2.76 \qquad (13)$$
$$r^2 = 0.1885;\; sd = 0.42;\; n = 19;\; \psi = 0.93$$

$$\log k_2 = 1.48\,(\pm 0.22)\,B - 3.43 \qquad (14)$$
$$r^2 = 0.7241;\; sd = 0.25;\; n = 19;\; \psi = 0.54$$

$$\log k_2 = 1.47 \pm 0.04\,(A + B) - 3.83 \qquad (15)$$
$$r^2 = 0.9847;\; sd = 0.06;\; n = 19;\; \psi = 0.13$$

The rates of oxidation of methionine in different solvents show an excellent correlation with Swain's equation with both the cation- and anion- solvating powers playing significant roles, though the contribution of the cation-solvation is slightly more than that of the anion-solvation. The solvent polarity, represented by (A + B), also accounted for *ca.* 98% of the data. However, the correlations individually with A and B were poor. In view of the fact that solvent polarity is able to account for *ca.* 98% 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 linear ($r^2 = 0.4797$; sd = 0.34; $\psi = 0.74$).

The observed solvent effect points to a transition state more polar than the reactant state. Further, the formation of a dipolar transition state, similar to those of S_N2 reactions, is indicated by the major role of both anion- and cation-solvating powers. However, the solvent effect may also be explained assuming that the oxidant and the intermediate complex exist as ion-pair in non-polar solvent like cyclohexane and be considerably dissociated in more polar solvents.

MECHANISM

In view of the absence of any effect of radical scavenger, acrylonitrile, on the reaction rate and recovery of unchanged BHT, it is unlikely that a one-electron oxidation giving rise to free

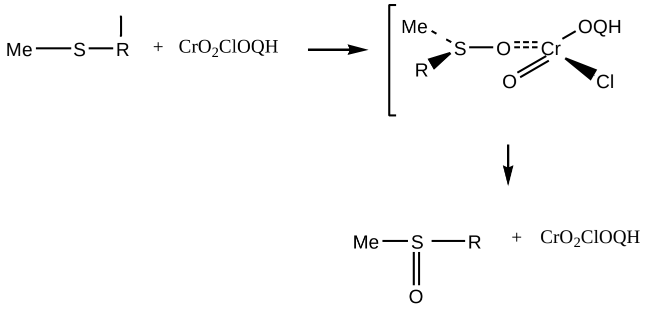
radicals is operative in this oxidation reaction. The observed Michaelis – Menten type of kinetics observed with respect to methionine, suggests the formation of 1:1 complex of QCC and Met in a rapid pre-equilibrium. With present set of data, it is difficult to state the definite nature of the intermediate complex. The experimental results can be accounted for in terms of electrophilic attack of methionine-sulphur at the metal *via* an intermediate complex. Transfer of an unshared pair of electrons to an empty d orbital of the metal resulted in the formation of a coordinate bond. The formation of intermediate is likely to undergo a further rapid reaction in which the incipient.
It is of interest to compare here the mode of oxidation of methionine by PFC,[16] pyridinium chlorochromate (PCC),[17] pyridinium bromochromate (PBC)[18] and QCC. The oxidation by PFC and PBC presented a similar kinetic picture, i.e. the reactions are of first order with respect to the reductants. While in the oxidation by PCC and QCC, Michaelis-Menten type kinetics was observed with respect to the reductants. It is possible that the values of the formation constants for the reductant-PFC/PBC complexes are very low. This resulted in the observation of second order kinetics. No explanation of the difference is available presently. Solvent effects and the dependence of the hydrogen ions are of similar nature in all these reactions, for which essentially similar mechanisms have been proposed.

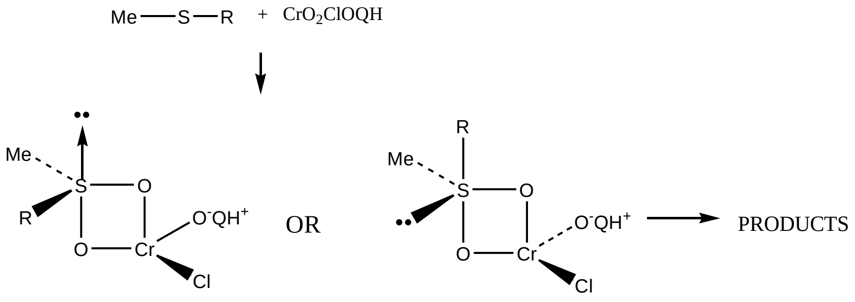
APPLICATIONS

A suitable mechanism can be suggested by this Study.

CONCLUSION

The oxidation of DL-methionine involves a rate-determining electrophilic attack of methionine sulfur at the metal *via* an intermediate complex. Both deprotonated and protonated forms of QCC are reactive oxidizing species.





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