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Oxidation of Methionine by Dabco Ammonium Chlorochromate: A Kinetic Study

Abstract

In dimethylsulphoxide (DMSO), the oxidation of methionine (Met) by dabco ammonium chlorochromate (DACC), leads to the formation of the corresponding sulphoxide. The reaction is of the first order regarding DACC. Michaelis-Menten type kinetics were ascertained regarding methionine. The reaction was catalyzed by hydrogen ions. The hydrogen-ion dependence have the form: $k_{obs} = a + b\,[H^+]$. The oxidation of methionine was examined in nineteen different organic solvents. By Kamlet's and Swain's multiparametric equations, the solvent effect was evaluated, which determined the importance of the cation-solvating power of the solvent. A best-suited mechanism has thus been postulated.

Keywords: Oxidation, Methionine, Mechanism, Solvent Effect.

Introduction

In synthetic organic chemistry, Cr (VI) salts have long been used as oxidizing reagents. However, these salts are rather drastic in nature and are non-selective oxidants. Miscibility is a problem with these salts as they are insoluble in most of the organic solvents. Thus to overcome these limitations, various organic derivatives of Cr (VI) have been prepared and used in organic synthesis as mild and selective oxidants in non-aqueous solvents[1-5]. Already several studies have been reported related to kinetic and mechanistic expressions of the oxidation by halochromates[6-17]. It is now recognized that the mode of oxidation depends upon the nature of the 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 various oxidants due to the electron-rich sulphur center which is easily oxidisable.Therefore, in continuation of our prior work, we report here the kinetics of oxidation of DL-methionine by DACC in dimethylsulphoxide (DMSO) as a solvent.

Aim of the Study

The main objective of the study is to determine the kinetic parameters like rate laws, effect of temperature, effect of catalysts, kinetic isotope effect, effect of pH, solvent effect, etc. To propose a suitable mechanism for the reaction.

Review of Literature

The oxidation of various organic compounds by QFC[2], PFC[3,4], QDC[5], QBC[6], BIFC[7,8], MFC[9-12], MCC[13], IFC[14], BPCC[15], TPSD[16], PBC[17],TEACC[22,23], andIDC[24,25]have been reported. But there is no report on oxidation of DL-methionine by DACC. In consideration of prior work, we have embarked upon an investigation on the kinetic and thermodynamic expression of this reaction.

Materials and Methods

Materials

DACC was prepared by the method reported[18] and an iodometric method was used to check its purity. Methionine (Merck) was commercially available. Toluene-p-sulphonic acid (TsOH) was used as a source of hydrogen ions due to the non-aqueous nature of the solvent. The rest of the solvents were purified by the usual methods [19].

Kinetic Measurements

By keeping an excess (×10 or greater) of the reductant over the DACC, conditions of pseudo-first order were achieved. The solvent used was DMSO, unless specifiedotherwise. All the reactions were studied at a constant temperature (±0.1 K). The reactions were followed spectrophotometrically by monitoring the decrease in the concentration of

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DACC used for no less than three half-lives. The pseudo-first order rate constant, k_{obs}, was figured out from the linear ($r^2 > 0.995$) plots of log [DACC] against time. The second order rate constant, k_2, was figured out from the relation: $k_2 = k_{obs} / $ [reductant]. All the experiments were carried out in the absence of TsOH, apart from those for studying the effect of hydrogen ions.

Results and Discussion
Stoichiometry

The oxidation of methionine by DACC resulted in the formation of the analogous sulfoxide. The overall reaction may then, be represented as equation (1).

$$R\!-\!S\!-\!R \xrightarrow{\text{DACC}} R\!-\!\underset{\underset{O}{\|}}{S}\!-\!R \qquad \text{... (1)}$$
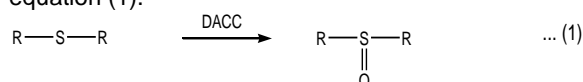
Where R is -CH$_2$-CH$_2$-CH(NH$_2$)COOH

Here, the DACC undergoes a two-electron change. This is in reference to the earlier observations with structurally similar halochromates. It has already been proved that both the pyridiniumfluorochromate (PFC)[4] and the imidazoliumfluorochromate (IFC)[14] act as two electron oxidants and are reduced to chromium(IV) species.
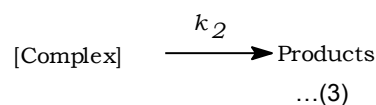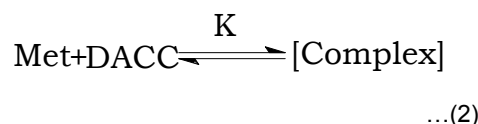
Rate Laws

The oxidation of methionine by DACC is predicted to be first order with respect to DACC, both regarding to time (as evidence by good fits of log [DACC] versus time plot) and concentration (as shown by time order rate-coefficients being independent of initial [DACC]). The variation in the concentration of methionine showed that the reaction rate increased with an increase in the [methionine] but not linearly.

The Figures1 show a representative kinetic run. The various rate constants of the oxidation of DL-methionine are given in Table 1.

The order of reaction is less than one as regards the methionine. A plot of $^1/k_{obs}$ against ^{1}/[Methionine] is linear (r> 0.995) with an intercept on the rate ordinate (Figure 2). Thus, Michaelis-Menten type kinetics are observed as regards the methionine. This leads to the postulation of the following overall mechanism (2) and (3) and the rate law (4).

$$\text{Met+DACC} \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \text{[Complex]} \qquad \ldots(2)$$

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

$$\text{Rate} = \frac{k_2 K[\text{Met}][\text{DACC}]}{(1+K[\text{Met}])} \qquad \ldots(4)$$

The dependence of the rate of the reaction on the concentration of methionine was determined at diverse temperatures. The value of equilibrium constant, K and of the rate constants k_2, were figured out from the double reciprocal plots. The thermodynamic parameters of the complex formation and the activation parameters of the decomposition of the complex were calculated from the value of K and k_2 respectively (Table 2 to 5).
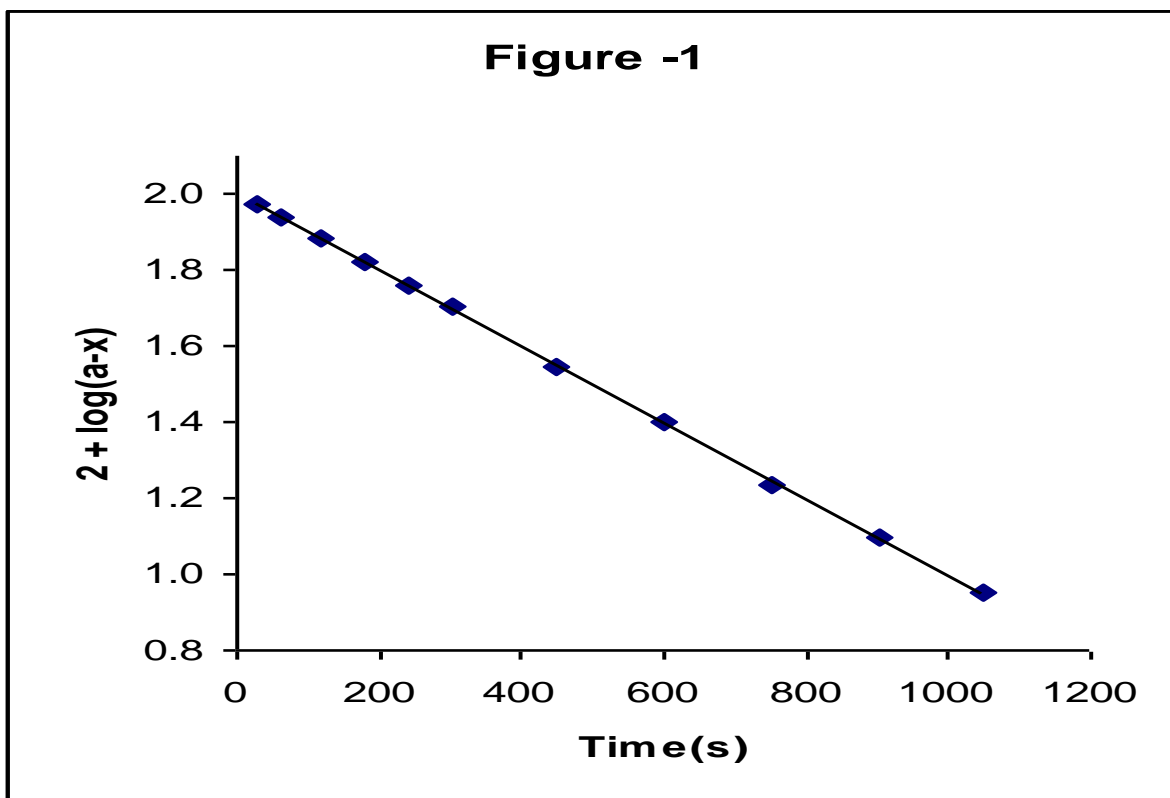
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Figure 1: Oxidation of Methionine by DACC: A Typical Kinetic Run

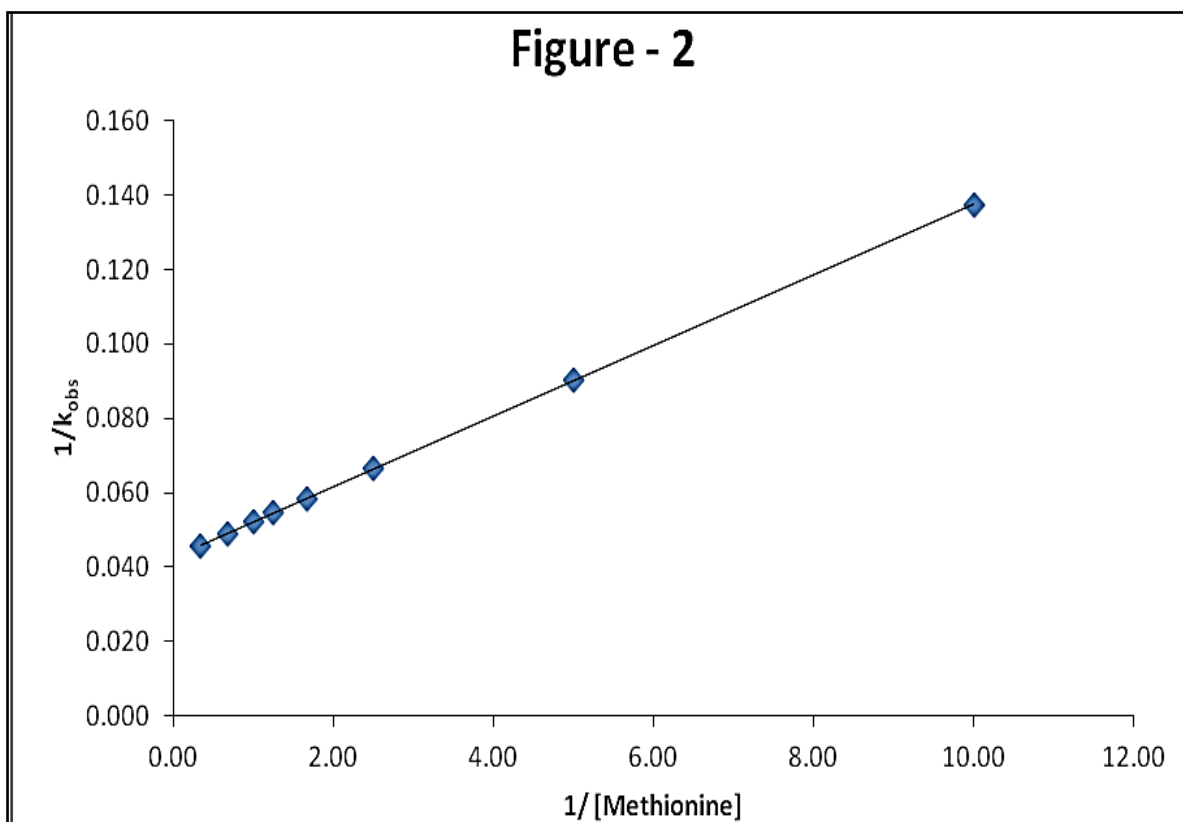Figure 2: Oxidation of Methionine by DACC: A Double Reciprocal Plot

Table 1: **Rate Constants for the Oxidation of DL-methionine by DACC at 308 K**

10^3 [DACC] (mol dm^{-3})	[Met] (mol dm^{-3})	[TsOH] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})
1.00	0.10	0.00	6.99
1.00	0.20	0.00	10.9
1.00	0.40	0.00	14.8
1.00	0.60	0.00	16.7
1.00	0.80	0.00	17.9
1.00	1.00	0.00	18.8
1.00	1.50	0.00	20.3
1.00	3.00	0.00	22.0
2.00	0.40	0.00	14.9
4.00	0.40	0.00	14.2
6.00	0.40	0.00	15.6
8.00	0.40	0.00	14.2
1.00	0.10	0.10	8.50
1.00	0.10	0.20	10.7
1.00	0.10	0.40	12.4
1.00	0.10	0.60	14.9
1.00	0.10	0.80	17.8
1.00	0.10	1.00	20.6
1.00	0.20	0.00	11.6*

* contained 0.001 mol dm^{-3} acrylonitrile.

Table 2: Formation Constants of the Oxidation of DACC-Met Complexes

K (dm^3 mol^{-1})			
288 K	298 K	308 K	318 K
6.54	5.23	4.31	3.57

Table 3: Thermodynamic parameters of the oxidation of DACC-Met complexes

-ΔH (kJ mol^{-1})	-ΔS (J mol^{-1} K^{-1})	-ΔG (kJ mol^{-1})
15.1± 0.9	29± 3	6.58± 0.6

Table 4: Rate constants of the decomposition of DACC-Met complexes

10^4 k_2/ (dm^3 mol^{-1} s^{-1})			
288 K	298 K	308 K	318 K
4.84	10.5	22.9	47.2

Table 5: Activation parameters of the decomposition of DACC-Met complexes

ΔH* (kJ mol^{-1})	-ΔS* (J mol^{-1} K^{-1})	ΔG* (kJ mol^{-1})
55.4± 0.2	114± 3	89.5± 0.2

Test for Free Radicals

The oxidation of unsaturated acids, by DACC, in an atmosphere of nitrogen failed to stimulate the polymerisation of acrylonitrile. Then the addition of acrylonitrile also did not affect the rate of reaction (Table 1). We further confirmed 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-4methylphenol (butylatedhydroxytoluene or BHT). It is observed that BHT is recovered unchanged, almost quantitatively.

Effect of Acidity

P-toluene sulphonic acid (TsOH) is used as a source of hydrogen ions due to the non-aqueous nature of the solvent (Table 1). It is detected that the reaction is catalyzed by hydrogen ions. The hydrogen–ion dependence can be shown in form of equation (5) as follows:

$$k_{obs} = a + b \left[H^+ \right] \qquad …(5)$$

The value of a andb are 7.54± 0.30 x 10^{-4} s^{-1} and 13.1± 0.50 x10^{-4} mol^{-1} dm^3 s^{-1} respectively (r^2=0.9942).

Solvent Effect

In nineteen different organic solvents, the rates of the oxidation of the methionine by DACC were studied. There was no reaction with the chosen solvents. The kinetics were similar in all the solvents. The value of formation constants are almost similar but value of rate constants are varied with the solvents. The values of K and k_2 are recorded in Table 6.

Table 6: Effect of solvents on the oxidation of methionine by DACC at 298 K

Solvents	K (dm^{-3} mol^{-1})	$10^5 k_2$ (s^{-1})
Chloroform	6.12	66.9
1,2-Dichloroethane	5.02	88.6
Dichloromethane	5.86	73.8
DMSO	4.53	236
Acetone	5.41	58.6
DMF	5.53	116
Butanone	6.29	41.5
Nitrobenzene	4.50	95.8
Benzene	5.51	22.9
Cyclohexane	5.47	1.84
Toluene	5.62	14.5
Acetophenone	5.49	78.9
THF	5.53	27.1
t-butyl alcohol	4.19	34.1
1,4-Dioxane	4.36	29.7
1,2-Dimethoxyethane	4.84	18.6
Carbon disulfide	5.49	7.86
Acetic acid	5.33	25.4
Ethyl acetate	5.02	23.0

Linear solvation energy relationship equation (6) of Kamatet al[20] was used to correlate the rate constants of the oxidation k_2, in eighteen solvents (CS$_2$ was not considered, as the complete range of solvent parameters was not available).

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

In this equation, π^* represents the solvent polarity, β is the hydrogen bond acceptor basicity and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of 18 solvents, 12 have a value of zero for α. Correlation analysis in terms of equation (6), a biparametric equation involving π^* and β, and separately with π^* and β are given below:

$$\log k_2 = -3.63 + 1.79 (\pm0.15) \pi^* + 0.15 (\pm0.13) \beta + 0.18 (\pm0.12)\alpha \qquad …(7)$$

$R^2 = 0.8683$; sd = 0.17; n = 18; $\psi = 0.36$

$$\log k_2 = -3.60 + 1.72 (\pm 0.15) \pi^* + 0.22 (\pm 0.13) \beta \qquad …(8)$$

$R^2 = 0.8759$; sd = 0.17; n = 18; $\psi = 0.36$

$$\log k_2 = -3.61 + 1.78 (\pm0.18) \pi^* \qquad …(9)$$

$r^2 = 0.8581$; sd = 0.18; n = 18; $\psi = 0.39$

$$\log k_2 = -2.61 + 0.52 (\pm0.37) \beta \qquad …(10)$$

$r^2 = 0.1103$; sd = 0.45; n = 18; $\psi = 1.00$

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

Kamlet's[20] triparametric equation explains ca. 89% of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory (cf. equation 7). The major contribution is of solvent polarity. It alone accounted for Ca. 86% of the data. Both β and α play relatively minor roles. Swain's equation[21] of cation and anion solvating concept of the solvents was used to analyzed the solvent effect as well.

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

Here A represents the anion solvating power of the solvent and B is 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).

$$\log k_2 = 1.13 (\pm0.03) A + 1.70 (\pm 0.04) B - 3.87 \qquad …(12)$$

$R^2 = 0.9971$; sd = 0.03; n = 19; $\psi = 0.07$

$$\log k_2 = 0.89 (\pm0.54) A - 2.70 \qquad …(13)$$

$r^2 = 0.1296$; sd = 0.45; n = 19; $\psi = 0.96$

$$\log k_2 = 1.61 (\pm0.17) B - 3.50 \qquad …(14)$$

$r^2 = 0.7981$; sd = 0.22; n = 19; $\psi = 0.47$

$$\log k_2 = 1.51 \pm 0.06 (A+B) - 3.85 \qquad …(15)$$

$r^2 = 0.9680$; sd = 0.10; n = 19; $\psi = 0.21$

Oxidation of methionine by DACC in different solvents showed an excellent correlation in Swain's equation. Cation and anion solvating power have a significant role, though the contribution of the cation–solvation is slightly more than that of anion–salvation. The solvent polarity, represented by (A+B), also accounted for *ca.* 97% of the data. However, the correlation 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. The observed solvent effect indicated that the transition state is more polar than the reactant state. Further, the formation of a dipolar transition state, similar to those of S$_N$^{2} 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 a non-polar solvent like cyclohexane and be considerably dissociated in more polar solvents.

Mechanism

In consideration of the absence of any effect of the radical scavenger, acrylonitrile, on the reaction rate and recovery of unchanged BHT, it is improbable that one-electron oxidation is operative in this oxidation reaction, giving rise to free radicals. The experimental results can be considered in terms of electrophilic oxygen transfer from DACC to the methionine–sulphur via an intermediate complex. An

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$S_N{}^2$ like transition state is backed by the observed solvent effect.

Conclusion

In the oxidation of DL-methionine by dabco ammonium chlorochromate, the reaction was first order in respect of dabco ammonium chlorochromate and Michaelis-Menten type kinetics was observed in respect of methionine. The free radical reaction was absent. The rate of reaction increases on the increasing concentration of hydrogen ions. The rate of reaction is varied with the nature of the solvent.

Endnotes

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