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ORIGINAL ARTICLE

Oxidation of methionine by tetraethylammonium chlorochromate in non-aqueous media – A kinetic and mechanistic study

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Abstract The kinetics of oxidation of methionine (Met) by tetraethylammonium chlorochromate (TEACC) in dimethyl sulfoxide (DMSO) leads to the formation of the corresponding sulfoxide. The reaction is first order each in Met and TEACC. The reaction is catalyzed by hydrogen ions. The hydrogen ion dependence has the form : $k_{obs} = a + b\,[H^+]$. The reaction rate has been determined at different temperatures and activation parameters are calculated. The solvent effect has been analyzed using Kamlet's multi parametric equation. A correlation of data with Kamlet–Taft solvatochromic parameters (α, β, π^*) suggests that the specific solute–solvent interactions play a major role in governing the reactivity. The reaction does not induce polymerization of acrylonitrile. A suitable mechanism has been proposed.

1. Introduction

Selective oxidation of organic compounds under non-aqueous conditions is an important reaction in synthetic organic chemistry. Oxidation kinetics has received considerable attention due to the wide range of biological processes in which metal ions participate. Chromium(VI) acts as an efficient catalyst in redox reactions. A number of new chromium(VI) containing compounds like pyridinium chlorochromate (Corey and Suggs, 1975), tributylammonium chlorochromate (Mansoor and Shafi, 2010a), tripropylammonium fluorochromate (Mansoor and Shafi, 2010b), pyridinium fluorochromate (Bhattacharjee et al., 1982), imidazolium fluorochromate (Pandurangan et al., 1999) and isoquinolinium bromochromate (Vibhute et al., 2009) have been used to study the kinetics and mechanism of various organic compounds.

Extensive studies on the mechanism of the oxidation of methionine by several oxidants have been reported (Satsangi et al., 1995; Bhuvaneshwari and Elango, 2008; Sharma et al., 1997; Pandeeswaran et al., 2005; Khan, 1997; Meenashisundaram and Vinothini, 2003). Methionine is an intermediate in the

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biosynthesis of cysteine, carnitine, taurine, lecithin, phosphatidylcholine and other phospholipids. It is a naturally occurring sulfur containing amino acid, has three coordination sites : at the N, O and S centers. Sulfur has been established as the most susceptible to attack by chromium(VI), where the formation of an intermediate (chromate ester) provides a low energy path for electron transfer (Olatunji and McAuley, 1997a,b; McAuley and McCann, 1975). Methionine is a methyl donor and this process in the body is activated by adenosine triphosphate (ATP) and a liver enzyme such as phosphatase or dehydrogenase (Saxena et al., 1982). Active methionine can transfer its methyl group to a variety of compounds and the high energy S-methyl bond is the prime reason for this behavior.

Amino acids are susceptible to oxidation by various forms of reactive oxygen species (ROS) and the oxidation reaction may proceed through one or two electron transfer depending on the nature of the oxidant (Alfassi, 1999; Townsend et al., 2004; Lai et al., 2002). However, studies show that when an oxidation sensitive sulfide is located in a biomolecule such as methionine residue in a peptide or protein, the redox reaction is affected by amino and carboxyl groups, present in close proximity to sulfide function (Schfneich, 2005; Marciniak et al., 1995; Pogocki et al., 2001). Because of its susceptibility to oxidation, methionine (Met) is thought to play a key role in the migration of unpaired electron in peptides and proteins.

It is suggested that Met can serve as an endogenous antioxidant in proteins and Met oxidation to Met sulfoxide has a regulatory function, based on its potential reversion by the enzyme methionine sulfoxide reductase (Msr) (Stadtman et al., 2005). The one-electron oxidation of Met to the Met sulfur radical cation, may play an important role for protein oxidation during conditions of oxidative stress and biological aging (Miller et al., 1998; Yatin et al., 1999). Because of these reasons the oxidation of methionine and methionine containing peptides has been the subject of many studies (Perrin and Koppenol, 2000; Hong and Schoneich, 2001; Whitelegge et al., 2000; Fonkeng et al., 1998). In vivo oxidation of Met residues leads to the formation of Met sulfoxide and most cells containing methionine sulfoxide reductase, catalyze the thioredoxin-dependent reduction of Met sulfoxide residues back to methionine residues (Stadtman, 2002). Moreover, increase in the levels of Met sulfoxide resulted in the lower abundance of active Msr and/or the required cofactors as a consequence of pathologies and to Alzheimer's diseases (Weissbach et al., 2005).

Literature survey reveals that no report is available on the kinetics of oxidation of methionine by TEACC. We report here, the kinetics and mechanism of the oxidation of methionine by TEACC in dimethyl sulfoxide (DMSO) as solvent, with the view to obtaining the utility of solvent variation studies in the understanding of the mechanism of this biologically important amino acid, because it may reveal the mechanism of amino acid metabolism.

2. Materials and methods

2.1. Reagents

Tetraethylammoniumchloride and chromium trioxide were obtained from Fluka (Buchs, Switzerland). DL-Methionine (E Merck, Germany) was used as received. TEACC was prepared by the reported method (Pandurangan and Murugesan, 1996) and its purity was checked by an iodometric method. Because of the non-aqueous nature of the solvent, *p*-toluene sulfonic acid (TsOH) was used as a source of hydrogen ions. Solvents were purified by the usual method (Weissberger and Prabankar, 1995).

3. Experimental procedures

3.1. Kinetic measurements

Reactions were studied under pseudo-first-order conditions by keeping a large excess of Met (×15 or more) over TEACC. The solvent was DMSO, unless mentioned otherwise. The studies were carried out in the temperature range of 298–313 K and were followed up to 80% completion by monitoring the decrease in [TEACC] at 364 nm spectrophotometrically. The pseudo-first order rate constants, k_{obs} were computed from linear ($r > 0.990$) least-square plots of log [TEACC] versus time. Duplicate kinetic runs showed that the rate constants were reproducible within ±3%. The second order rate constants k_2 were computed from the relation $k_2 = k_{obs}/[\mathrm{Met}]$.

3.2. Data analysis

Data analysis was performed using Microcal Origin (version 6.0) computer software. The goodness of the fit is discussed using the correlation coefficients and standard deviations.

4. Results and discussion

4.1. Stoichiometry and product analysis

The stoichiometry of the reaction was determined by performing the several sets of experiments with varying amounts of TEACC largely in excess over methionine. The disappearance of TEACC was monitored until constant titer values were obtained.

$$\begin{aligned} &\mathrm{Me-S-R + O_2CrClO^-N^+Et_4} \\ &\quad \rightarrow \mathrm{Me-SO-R + OCrClO^-N^+Et_4} \\ &\quad (\mathrm{R = -CH_2CH_2CH(NH_2)COOH}) \end{aligned} \tag{1}$$

The reaction mixture was allowed to stand for a few hours. Then, sodium bicarbonate was added and stirred vigorously, followed by drop wise addition of benzoyl chloride solution. The precipitate *N*-benzoyl methionine sulfoxide was confirmed by its m.p. 183 °C (Goswami et al., 1981). The procedure is similar to the one employed in the oxidation of L-methionine by chromium(VI) (Olatunji and Ayoko, 1988). Acetone–ethanol mixture (1:1) added to the reaction mixture resulted in the precipitate of methionine sulfoxide, which was identified by is m.p. 238 °C (Natile et al., 1976). The yield of sulfoxide was 91%.

4.2. Order of reaction

The oxidation of methionine with TEACC yields sulfoxide. The rate of oxidation was found to be first order in [Met]. Linear plots of log k_1 versus log [Met] with unit slope demonstrate

Table 1 Effect of varying the concentration of [Met], [TEACC] and [H$^+$] on the rate of reaction at 303 K.

10^3 [TEACC] (mol dm^{-3})	10^2 [Met] (mol dm^{-3})	[TsOH] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
0.5	2.0	0.0	15.88
1.0	2.0	0.0	16.04
1.5	2.0	0.0	16.18
2.0	2.0	0.0	16.38
2.5	2.0	0.0	16.24
1.0	4.0	0.0	31.80
1.0	6.0	0.0	46.90
1.0	8.0	0.0	63.12
1.0	10.0	0.0	79.26
1.0	2.0	0.1	17.38
1.0	2.0	0.2	21.12
1.0	2.0	0.4	24.68
1.0	2.0	0.6	28.72
1.0	2.0	0.8	33.08
1.0	2.0	0.0	15.88[a]
1.0	2.0	0.0	9.88[b]

[a] Contained 0.001 mol dm^{-3} acrylonitrile.
[b] In the presence of 0.003 mol dm^{-3} Mn(II).

the first-order dependence of the rate on [Met]. The near constancy in the values of k_1 irrespective of the concentration of the TEACC confirms the first-order dependence on TEACC (Table 1).

4.3. Effect of acidity

The reaction is catalyzed by hydrogen ions (Table 1). The hydrogen ion dependence has the following form:

$$k_{obs} = a + b[\mathrm{H}^+] \tag{2}$$

The values of a and b, for methionine at 303 K are 16.01 ± 0.2×10^{-4} s^{-1} and 21.42 ± 0.5×10^{-4} mol^{-1} dm^3 s^{-1}, respectively (r^2 = 0.997).

The observed hydrogen ion dependence suggests that the reaction follows two mechanistic pathways, one acid-independent another acid-dependent. The acid-catalysis may well be attributed to a protonation of TEACC to give a stronger oxidant and electrophile.

$$\mathrm{O_2CrClO^-N^+Et_4} + \mathrm{H^+} \rightleftharpoons \mathrm{(HO)Cr^+OClO^-N^+Et_4} \tag{3}$$

The formation of a protonated Cr(VI) species has earlier been postulated in the reactions of α-hydroxy acids and TEACC (Swami et al., 2010).

4.4. Induced polymerization

The oxidation of Met in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile. Furthermore, the rate of oxidation decreased with the addition of Mn(II) (Table 1). Therefore, a one-electron oxidation giving rise to free radicals is unlikely.

4.5. Thermodynamic parameters

The kinetics of oxidation of methionine was studied at four different temperatures *viz*., 298, 303, 308 and 313 K. The second order rate constants were calculated (Table 2). The Arrhenius plot of $\log k_2$ versus $1/T$ is found to be linear. The enthalpy of activation, entropy of activation and free energy of activation were calculated from k_2 at 298, 303, 308 and 313 K using the Eyring relationship by the method of least square and presented in Table 2. The entropy of activation is negative for methionine. The negative entropy of activation in conjunction with other experimental data supports the mechanism outlined in (Scheme 1).

4.6. Effect of solvent

The rate of oxidation of methionine was determined in 19 different organic solvents. The choice of the solvents was limited by the solubility of TEACC and its reactivity with methionine. There was no noticeable reaction with the solvents chosen. The values of k_2 at 303 K are recorded in Table 3.

4.7. Solvent-reactivity correlation

The influence of solvent on the rate of any reaction can be described in terms of solvation which is a stabilization process. Two view points have been established on the solvation phenomenon. According to the first, a solvent is considered as a homogeneous continuum which surrounds the solute molecules and exerts long range interactions. The strength of these interactions with the solute molecules is described in terms of macroscopic physical properties of the solvent like dielectric constant (ε) and refractive index (η). According to the second view point, a solvent is considered to be anisotropic and inhomogeneous which exerts short range forces on the solute molecules. These forces are chemical in nature, and result in the formation of solvation complexes through donor–acceptor bonds which are localized and directed in space. The strength of these interactions is described in terms of solvation parameters namely hydrogen bond donor acidity (α), hydrogen bond acceptor basicity (β), etc. Thus the solvent can solvate the solute by exhibiting any of these interactions with the specific sites in the solute. Hence, the effect of solvent on the rate of the reaction can be described in terms of multiparametric equation which involves different solvation parameters given by Kamlet–Taft.

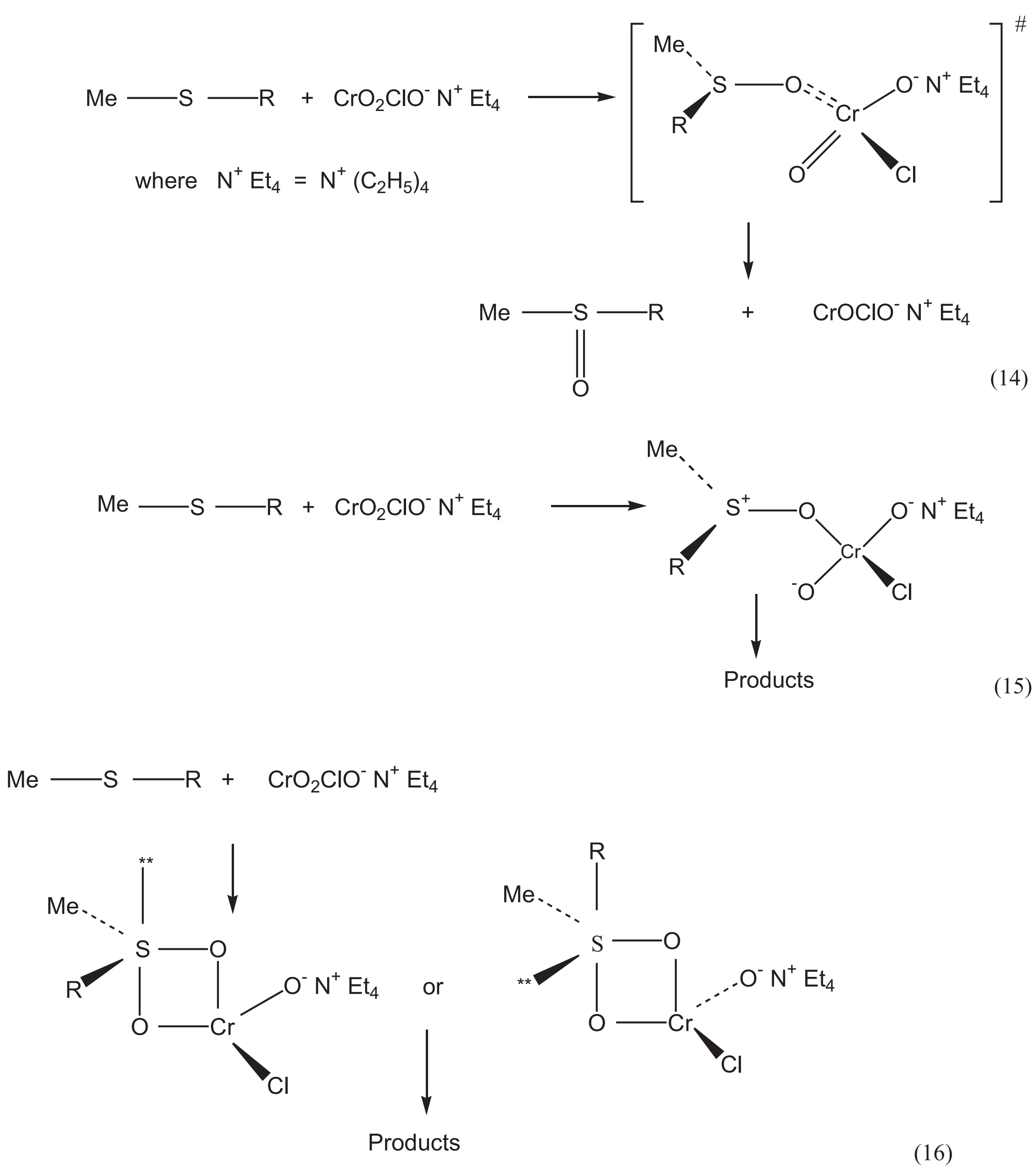
4.7.1. The Kamlet–Taft method for the examination of solvent effect

In order to obtain a deeper insight into the various solvent–solvent–solute interactions, which influence reactivity, the solva-

Table 2 Activation parameters and second order rate constants for the oxidation of methionine by TEACC.

Substrate	$10^2 \times k_2$, dm^3 mol^{-1} s^{-1}				$\Delta H^\#$ (kJmol^{-1})	$-\Delta S^\#$ (J K^{-1} mol^{-1})	$\Delta G^\#$ (kJmol^{-1})
	298 K	303 K	308 K	313 K			
Methionine	5.62	8.02	0.82	14.00	44.62 ± 1.3	119.11 ± 4	80.52 ± 2

[Met] = 2.0×10^{-2} M; [TEACC] = 1.0×10^{-3} M.



Scheme 1 Mechanism for the oxidation of methionine by TEACC.

Table 3 Second-order rate constants for the oxidation of Methionine by TEACC at 303 K in various solvents.

Solvents	$k_2 10^4$ (dm^{-3} mol^{-1} s^{-1})	Solvents	$k_2 10^3$ (dm^{-3} mol^{-1} s^{-1})
Chloroform	35.8	Toluene	8.7
1,2-Dichloroethane	29.3	Acetophenone	30.5
Dichloromethane	34.0	THF	15.0
DMSO	80.2	*tert*-Butyl alcohol	22.0
Acetone	27.0	1,4-Dioxane	16.7
DMF	43.9	1,2-Dimethoxyethane	10.0
Butanone	22.7	Carbon disulfide	5.7
Nitrobenzene	31.7	Acetic acid	13.0
Benzene	10.9	Ethyl acetate	13.3
Cyclohexane	1.7		

tochromic comparison method developed by Kamlet et al. (1983) has been used. This method may be used to unravel, quantify, correlate and rationalize multiple interacting solvent effects on reactivity. The kinetic data were correlated with the solvatochromic parameters α, β and π^* characteristic of different solvents in the form of following LSER:

$$\log k_2 = A_o + s\pi^* + b\beta + a\alpha \tag{4}$$

where π^* is an index of solvent dipolarity/polarizability, which is a measure of the ability of a solvent to stabilize a charge or a dipole by virtue of its dielectric effect. The parameter α represents the scale of the solvent HBD (hydrogen bond donor) acidity. It describes the ability of a solvent to donate a proton, or accept an electron pair in a solvent-to-solute hydrogen bond. The parameter β represents the scale of solvent HBA (hydrogen bond acceptor) basicity, in other words the ability of a solvent to donate an electron pair, or accept a proton in a solvent-to-solute hydrogen bond. A_o is the intercept term.

The rate constants of oxidation, k_2, in 18 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. (4) of Kamlet et al. (1983). It may be mentioned here that out of the 18 solvents, 12 have a value of zero for α. The second-order rate constant for the oxidation of methionine by TEACC in various solvents are presented in Table 3.

Kamlet et al. (1981) established that the effect of a solvent on the reaction rate should be given in terms of the following properties: (i) the behavior of the solvent as a dielectric, facilitating the separation of opposite charges in the transition state, (ii) the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond and thus stabilize the anion in transition state and (iii) the ability of the solvent to donate an electron pair and therefore stabilize the initial methionine, by way of a hydrogen bond. The parameter π^* is an appropriate measure of the first property, while the second and third properties are governed by the parameters α and β respectively. The solvent parameters (π^*, α and β) are taken from the literature (Kamlet et al., 1983) and are given in Table 4. The linear dependence (LSER) on the solvent properties was used to correlate and predict a wide variety of solvent effect.

Table 4 Solvent parameters (Kamlet et al., 1983).

Solvent	π^*	α	β
Chloroform	0.58	0.44	0.00
1,2-Dichloroethane	0.81	0.00	0.00
Dichloromethane	0.82	0.30	0.00
DMSO	1.00	0.00	0.76
Acetone	0.71	0.08	0.48
DMF	0.88	0.00	0.69
Butanone	0.67	0.06	0.48
Nitrobenzene	1.01	0.00	0.39
Benzene	0.59	0.00	0.10
Cyclohexane	0.00	0.00	0.00
Toluene	0.54	0.00	0.11
Acetophenone	0.90	–	0.49
THF	0.58	0.00	0.55
tert-Butyl alcohol	0.41	0.68	1.01
1,4-Dioxane	0.55	0.00	0.37
1,2-Dimethoxyethane	0.53	0.00	0.41
Carbon disulfide	–	–	–
Acetic acid	0.64	1.12	–
Ethyl acetate	0.55	0.00	0.45

In order to explain the kinetic results through the solvent polarity and basicity or acidity, the rate constants were correlated with the solvatochromic parameters π^*, α and β using total solvatochromic equation, Eq. (4). The correlation of kinetic data was realized by means of multiple linear regression analysis. It was found that the rate constants in 19 solvents showed satisfactory correlation with the π^*, α and β solvent parameters. The results of correlation analysis in terms of Eq. (4), a biparametric equation involving π^* and β are given below in Eqs. (5)–(8).

$$\log k_2 = -3.78 + (1.38 \pm 0.20)\pi^* + (0.14 \pm 0.08)\beta + (0.49 \pm 0.10)\alpha \tag{5}$$

$$R^2 = 0.9104;\ \mathrm{SD} = 0.11;\ n = 18;\ \psi = 0.25$$

$$\log k_2 = -3.59 + (1.21 \pm 0.15)\pi^* + (0.32 \pm 0.12)\beta \tag{6}$$

$$R^2 = 0.7614;\ \mathrm{SD} = 0.18;\ n = 18;\ \psi = 0.28$$

$$\log k_2 = -3.53 + (1.29 \pm 0.19)\pi^* \tag{7}$$

$$r^2 = 0.7228;\ \mathrm{SD} = 0.20;\ n = 18;\ \psi = 0.34$$

$$\log k_2 = -2.88 + (0.50 \pm 0.24)\beta \tag{8}$$

$$r^2 = 0.1622;\ \mathrm{SD} = 0.35;\ n = 18;\ \psi = 0.88$$

here n is the number of data points and ψ is the Exner's statistical parameter (Exner, 1966).

Kamlet's (Kamlet et al., 1983) triparametric equation explains *ca.* 91% of the effect of solvation on the oxidation. However, by Exner's criterion (Exner, 1966) the correlation is not even satisfactory (*cf.* Eq. (8)). The major contribution is of solvent polarity. It alone accounted for *ca.* 72% of the data. Both α and β play relatively minor roles.

4.7.2. The Swain's method for the examination of solvent effect

The data on solvent effect were analyzed in terms of Swain's equation (Swain et al., 1983) of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \tag{9}$$

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 analyzed in terms of Eq. (9), separately with A and B and with (A + B).

$$\log k_2 = (1.34 \pm 0.03)A + (1.15 \pm 0.02)B - 3.88 \tag{10}$$

$$R^2 = 0.9949;\ \mathrm{SD} = 0.04;\ n = 19;\ \psi = 0.06$$

$$\log k_2 = 1.18(\pm 0.39)A - 3.06 \tag{11}$$

$$r^2 = 0.3552;\ \mathrm{SD} = 0.08;\ n = 19;\ \psi = 0.68$$

$$\log k_2 = 1.05(\pm 0.26)B - 3.38 \tag{12}$$

$$r^2 = 0.5466;\ \mathrm{SD} = 0.19;\ n = 19;\ \psi = 0.45$$

$$\log k_2 = 1.22 \pm 0.04(A + B) - 3.85 \tag{13}$$

$$r^2 = 0.9876;\ SD = 0.08;\ n = 19;\ \psi = 0.06$$

The rates of oxidation of methionine in different solvents show an excellent correlation in Swain's equation (Eq. (10)) with both the cation and anion-solvating powers playing the major role, 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.* 99% 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 ($r^2 = 0.5876$; SD = 0.25; $n = 0.49$).

4.8. Mechanism of oxidation

In view of the absence of any effect of radical scavenger, acrylonitrile, on the reaction rate, it is unlikely that a one-electron reaction giving rise to free radicals, is operative in this oxidation. TsOH is a strong acid and is expected to be highly ionized in an aprotic polar solvent like DMSO. However, one cannot rule out the possibility of the formation of an ion pair. Therefore, the reactive oxidizing species in the catalyzed reaction may well be the ion pair. The experimental results can be accounted for in terms of rate-determining electrophilic oxygen transfer from TEACC to sulfide as Eq. (14), similar to that suggested for oxidations of sulfides and iodide ions by per iodate ion (Ruff and Kucsman, 1985) and for the oxidation of sulfides by pyridinium fluorochromate (Banerji, 1988) and morpholinium chlorochromate (Malani et al., 2009). The nucleophilic attack of a sulfide–sulfur on a TEACC oxygen can be viewed as an S_N2 reaction. An S_N2-like transition state is supported by the observed solvent effect. The solvent effect also supports a transition state depicted in Eq. (14), rather than a sulfonium ion as shown in Eq. (15).

The oxidation may involve a cyclic transition state as suggested in many reactions of Cr(VI) (Chang and Westheimer, 1960; Rocek and Westheimer, 1962). The cyclic transition state will be highly strained in view of the apical position of a lone pair of electrons or an alkyl group (Eq. 16). The steric requirements of the reaction (Eq. 16) would be higher than those of reaction (Eq. 14). The formation of cyclic transition state entails a more exacting specificity of orientation and should result in a much larger negative entropy of activation than that observed.

5. Conclusion

In this paper, kinetics and mechanism of oxidation of Met by TEACC is reported. The reaction is first order each in Met and TEACC. The reaction is catalyzed by hydrogen ions. Under the employed experimental conditions, methionine is oxidized to the corresponding sulfoxide stage only. Various thermodynamic parameters for the oxidation have been reported. Negative entropy of activation indicates a greater degree of ordering in the transition state than in the initial state, due to an increase in solvation during the activation process. The rate data show a satisfactory correlation with Kamlet–Taft solvatochromic parameters (α, β, π^*) which suggest that the specific solute–solvent interactions play a major role in governing the reactivity.

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