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ORIGINAL ARTICLE

Correlation analysis of reactivity in the oxidation of methionine by benzimidazolium fluorochromate in different mole fractions of acetic acid–water mixture

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Oxidation;
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Solvent effect

Abstract The kinetics of oxidation of methionine (Met) by benzimidazolium fluorochromate (BIFC) has been studied in the presence of chloroacetic acid. The reaction is first order with respect to methionine, BIFC and acid. The reaction rate has been determined at different temperatures and activation parameters calculated. With an increase in the mole fraction of acetic acid in its aqueous mixture, the rate increases. The solvent effect has been analyzed using the Kamlet's multi parametric equation. A correlation of data with the 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

The development of oxidizing agents based upon higher-valent transition metal oxo derivatives has been a subject of research in many laboratories and a host of such reagents derived from ruthenium, osmium, iron, manganese, molybdenum, vanadium and chromium have all proven to be capable of oxidation of organic substrates. In particular, there is continued interest in the development of new chromium(VI), Cr(VI) reagents for the effective and selective oxidation of organic substrates under mild conditions. A number of new Cr(VI) containing compounds like quinolinium fluorochromate (Dave et al., 2002) tributylammonium chlorochromate (Mansoor and Shafi, 2010a), quinolinium dichromate (Medien, 2003), tripropylammonium fluorochromate (Mansoor and Shafi, 2010b), imidazolium fluorochromate (Pandurangan et al., 1999), isoquinolinium bromochromate (Vibhute et al., 2009) tetrabutylammonium bromochromate (Ghammamy et al., 2007), tetraheptylammonium bromochromate (Ghammamy et al., 2009), tetrahexylammonium fluorochromate (Koohestani et al., 2008), tetramethylammonium fluorochromate (Sadeghy and Ghammamy, 2005) and tetraethyl ammonium bromochromate (Mansoor and Shafi, 2011) have been used

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to study the kinetics and mechanism of various organic compounds.

The oxidation of methionine (Met) plays an important role during biological conditions of oxidative stress as well as for protein stability (Venkataramanan et al., 2007). Oxidation of methionine has been studied extensively using different oxidants (Satsangi et al., 1995; Ghosh et al., 1999; Sharma et al., 1997; Pandeeswaran et al., 2005; Zaheer Khan, 1997; Meenashisundaram and Vinothini, 2003). Methionine (Met) is an important amino acid in human nutrition that is only available from food sources (Lee and Gladydhev, 2011). It is a versatile amino acid at the junction of several metabolic pathways. For example, Met (N-formylmethionine in prokaryotes) is used as the first (N-terminal) amino acid during translation and can often be a limiting factor in protein synthesis, especially under conditions of Met deficiency. Met is also a crucial metabolite that influences redox homeostasis through sulfur metabolism and the transsulfuration pathway (Metayer et al., 2008; Deth et al., 2008). Met is the source of several antioxidants and other sulfur compounds, which function in the defense against oxidative stress, such as glutathione (GSH), taurine, and cysteine (Cys), and therefore, Met is a core amino acid that supplies antioxidants to balance the cellular redox status against the attack by reactive oxygen species (ROS). In addition, S-adenosylmethionine (SAM), another key metabolite produced from Met, is a major methyl donor in cells and an epigenetic regulator (Waterland, 2006). Aerobic organisms generate ROS as products or by-products of mitochondrial respiration, xanthine oxidase, NADPH oxidase, and other metabolic processes and enzymes (Kowaltowski et al., 2009).

Accumulative post translational modification to proteins, mediated by the action of ROS, is thought to be one of the major causes of aging and age related diseases. Thus, mechanisms have evolved to prevent or reverse these protein modifications. While most protein damage by ROS is irreversible, methionine oxidation to proteins can be reversed by the methionine sulfoxide reductase (Msr) system, which consists of MsrA (that reduces *S*-MetO) and MsrB (that reduces *R*-MetO), thioredoxin reductase, thioredoxin, and NADPH (Moskovitz, 2005). ROS may damage macromolecules, such as proteins, lipids, and DNA, which leads to an increased incidence of disease and accelerated aging (Lovell and Markesbery, 2007; Valko et al., 2007). In the case of protein oxidation, all amino acids are subject to oxidative modification (Stadtman, 1993). However, Met is one of two common amino acids (together with Cys) that are most susceptible to oxidation by ROS, and therefore enzymatic systems evolved to counteract this damage. In addition, this amino acid may further contribute to antioxidant function when coupled with reductases (Dalle-Donne et al., 2002; Vogt, 1995). Interestingly, Met has a unique oxidation pattern in that two diastereomers are produced, which require separate enzyme systems for their reduction (Lee et al., 2009). Methionine sulfoxide is a major product of Met oxidation. Met is highly susceptible to oxidation by ROS and reactive nitrogen species (RNS) (Lavine, 1994). Generally, all amino acids are subject to free radical-mediated oxidation by radiation, metal catalyzed reactions, mitochondrial respiration, and many other processes generating ROS, but Met is among the most sensitive to oxidation. In the case of metal ion-catalyzed oxidation, α-carbon of amino acids, including that of Met, can undergo oxidative deamination (Stadtman and Berlett, 1991). However, it appears that only ~10% Met is converted to NH_4^+, $RCOO^-$, and O_2, whereas the major product of Met oxidation is Met sulfoxide.

Literature survey reveals that no report is available on the kinetics of oxidation of methionine by BIFC. In this article, the kinetics and mechanism of the oxidation of methionine by BIFC are reported, with the view to understand 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.

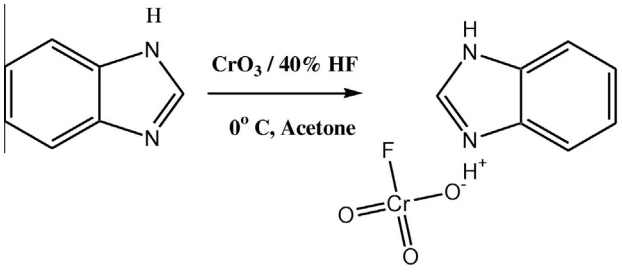
2. Experimental

2.1. Materials and methods

Benzimidazole and chromium trioxide were obtained from Fluka (Buchs, Switzerland). DL-methionine (E Merck, Germany) was used as received. The purities of reagents purchased are 99.9%. Acetic acid was purified by the standard method (Weissberger and Prabankar, 1995) and the fraction distilling at 118 °C was collected. All other chemicals used were of AnalaR grade.

2.2. Preparation of benzimidazolium fluorochromate

Benzimidazolium fluorochromate has been prepared from benzimidazole, 40% hydrofluoric acid and chromium trioxide in the molar ratio 1:1.3:1 at 0 °C. BIFC is obtained as yellow orange crystals. It is non-hygroscopic and light insensitive on storage (Sivamurugan et al., 2005). The purity of BIFC was checked by the iodometric method. The purity is 99.8%. The yield of BIFC was 86%.



Benzimidazole Benzimidazolium fluorochromate

(1)

2.3. Stoichiometry and product analysis

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

$$Me - S - R + O_2CrFOBIH \rightarrow Me - SO - R + OCrFOBIH \quad (2)$$

$(R = -CH_2CH_2CH(NH_2)COOH)$

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 sulphoxide 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 sulphoxide, which was identified by its m.p 238 °C (Natile et al., 1976). The yield of methionine sulphoxide was 92%.

2.4. Kinetic measurements

The pseudo-first-order conditions were attained by maintaining a large excess (×15 or more) of methionine over BIFC in the presence of chloroacetic acid. The solvent was double distilled water unless stated otherwise. The studies were carried out in the temperature range of 298–313 K. All the solutions were kept in a thermostat at constant temperature which was controlled using a thermostat of ±0.1 °C accuracy. The required volumes of these solutions for each run were mixed and 2 ml aliquots of the reaction mixture were pipetted out at convenient time intervals and quenched in 10 ml 2% KI solution and the liberated iodine was titrated against thiosulphate using starch as indicator. The pseudo-first-order rate constants were evaluated from log titre versus time plots. All the rate constants reported are an average of two or more determinations. The second order rate constant k_2, was obtained from the relation $k_2 = k_{obs}/[Met]$.

2.5. 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.

3. Results and discussion

3.1. Order of reaction

The oxidation of methionine with BIFC in the presence of chloroacetic acid yields methionine sulphoxide. The rate of oxidation was found to be first order in [Met]. Linear plots of 5 + log *kobs* versus 3 + log [Met] with unit slope demonstrate the first-order dependence of the rate on [Met] (Fig. 1). The near constancy in the values of k_1 irrespective of the concentration of the BIFC confirms the first order dependence on BIFC (Table 1).

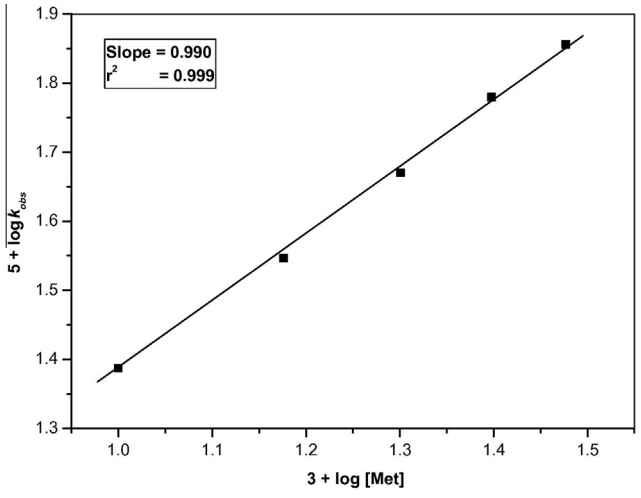


Figure 1 Order plot for the oxidation of methionine by benzimidazolium fluorochromate at 303 K.

The dependence of the reaction rate on the hydrogen ion concentration has been investigated at different initial concentrations of chloroacetic acid while keeping the concentrations of the other reactants constant. It may be seen that the rate of reaction increases linearly with an increase in the hydrogen ion concentration (Table 1). A plot of log k_1 versus log $[H^+]$ is linear with a unit slope. The reaction proceeds completely through an acid-catalyzed pathway (Bishoni et al., 1986). The acid catalysis may well be attributed to the protonation on BIFC to give a stronger oxidant and electrophile.

Therefore the rate law can be represented as:

$$-d[BIFC]/dt = k[Met][BIFC][H^+] \quad (3)$$

3.2. 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.

3.3. Effect of varying ionic strength

The oxidation of Met was carried out in the presence of sodium perchlorate (Table 2). There was no appreciable change

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

10^3 [BIFC] mol.dm^{-3}	10^2 [Met] mol.dm^{-3}	$[H^+]$ mol.dm^{-3}	10^4 *kobs* s^{-1}
0.5	2.0	0.2	4.60 ± 0.18
1.0	2.0	0.2	4.68 ± 0.12
1.5	2.0	0.2	4.66 ± 0.20
2.0	2.0	0.2	4.70 ± 0.08
2.5	2.0	0.2	4.68 ± 0.10
1.0	1.0	0.2	2.44 ± 0.04
1.0	1.5	0.2	3.52 ± 0.06
1.0	2.5	0.2	6.02 ± 0.16
1.0	3.0	0.2	7.18 ± 0.12
1.0	2.0	0.3	6.88 ± 0.14
1.0	2.0	0.4	8.88 ± 0.12
1.0	2.0	0.5	10.96 ± 0.18
1.0	2.0	0.6	13.08 ± 0.18
1.0	2.0	0.2	4.14 ± 0.06[a]
1.0	2.0	0.2	2.88 ± 0.03[b]

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

Table 2 Effect of added sodium perchlorate on the oxidation of methionine by BIFC at 303 K.

$[NaClO_4]$	0	0.01	0.015	0.02	0.025
$10^4\ k_1/s^{-1}$	4.68	4.40	4.38	4.52	4.28

[Met] = 2.0×10^{-2} mol.dm^{-3}; [BIFC] = 1.0×10^{-3} mol.dm^{-3}; $[H^+]$ = 0.2 mol.dm^{-3}.

Table 3 Rate constants and activation parameters for the oxidation of methionine by BIFC in various mole fractions of acetic acid.

Mole fraction of AcOH	$10^2 \times k_2$		$dm^3mol^{-1}s^{-1}$		$\Delta H^{\#}$ $kJmol^{-1}$	$-\Delta S^{\#}$ $JK^{-1}mol^{-1}$	$\Delta G^{\#}$ (303 K) $kJmol^{-1}$
	298 K	303 K	308 K	313 K			
0.0	1.73	2.34	3.20	4.40	45.6 ± 1.0	125.4 ± 3.0	83.6 ± 1.8
0.1	2.88	3.60	4.68	5.94	35.2 ± 1.0	156.6 ± 3.0	82.7 ± 1.9
0.2	3.08	4.05	5.26	6.84	38.5 ± 0.3	144.4 ± 1.0	82.2 ± 0.6
0.3	3.68	4.62	6.35	8.57	41.7 ± 2.0	132.8 ± 6.0	82.0 ± 3.8
0.4	4.53	6.03	8.02	10.66	41.6 ± 0.6	130.9 ± 1.8	81.2 ± 1.0
0.5	7.50	9.76	12.98	16.87	39.4 ± 0.7	133.8 ± 2.0	80.0 ± 1.3
0.6	10.16	13.41	17.56	23.36	40.8 ± 1.0	127.3 ± 3.0	79.3 ± 1.9
0.7	12.90	16.60	20.75	26.60	34.5 ± 0.8	145.7 ± 2.5	78.6 ± 1.5
0.8	14.70	20.10	27.20	35.90	43.7 ± 0.3	114.3 ± 0.8	78.3 ± 0.5
0.9	20.00	24.90	31.86	39.80	33.3 ± 0.8	146.8 ± 2.5	77.8 ± 1.5

[Met] = 2.0×10^{-2} mol.dm^{-3}; [BIFC] = 1.0×10^{-3} mol.dm^{-3}; [H^+] = 0.2 mol.dm^{-3}.

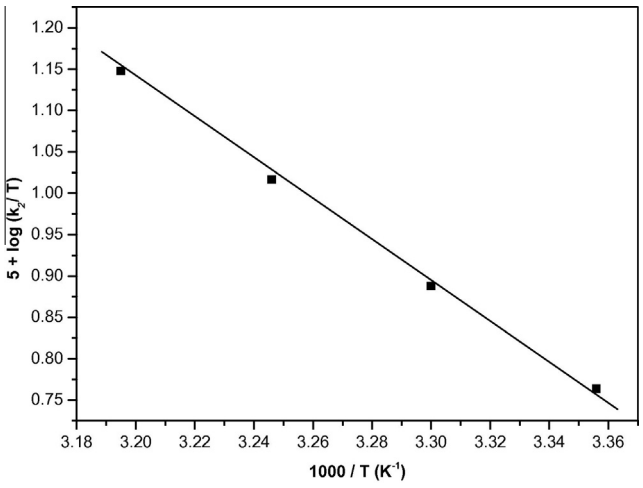
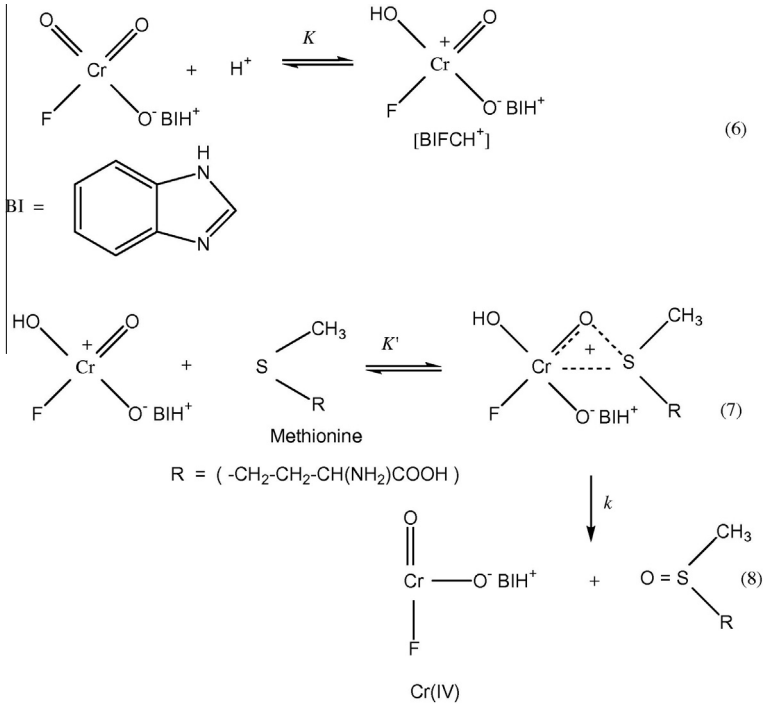


Figure 2 Eyring's plot for the oxidation of methionine by benzimidazolium fluorochromate.

in the rate with a change in ionic strength of the medium, affected by sodium perchlorate.

3.4. Thermodynamic parameters and isokinetic temperature

The activation parameters for the oxidation of methionine by BIFC were calculated from k_2 observed at four different temperatures *viz*., 298, 303, 308 and 313 K in presence of chloroacetic acid in ten different mole fractions. The values are presented in Table 3. The Arrhenius plot of 5 + log k_2/T versus 1000/T is found to be linear (Fig. 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). The reaction is neither isoenthalpic nor isoentropic but complies with the compensation law also known as isokinetic temperature. The isokinetic temperature is the temperature at which all compounds of the series react equally fast. Also, at the isokinetic temperature, the variation of substituent has no influence on



Scheme 1 Mechanism of oxidation of methionine by benzimidazolium fluorochromate.

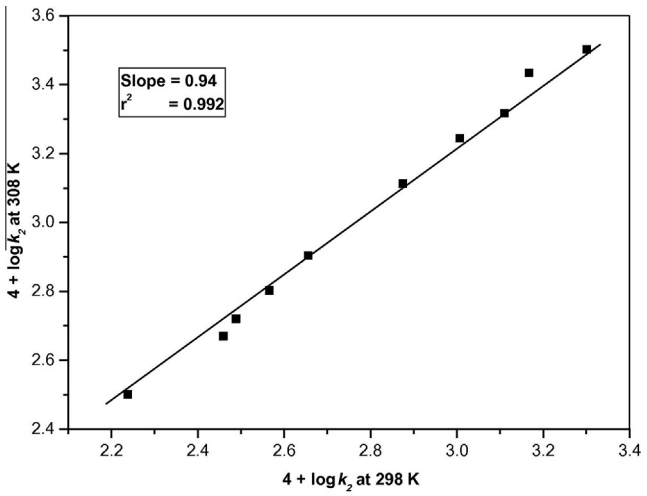


Figure 3 Exner's plot for oxidation of methionine by benzimidazolium fluorochromate between $4 + \log k_2$ (at 308 K) and $4 + \log k_2$ (at 298 K).

the free energy of activation. In an isoentropic reaction, the isokinetic temperature lies at infinite and only enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalpic series, and the reactivity is determined by the entropy of activation (Bhuvanseshwari and Elango, 2007). The isokinetic relationship is tested by plotting the logarithms of rate constants at two different temperatures ($T_2 > T_1$) against each other according to Eq. (4).

$$\log\ k(\text{at } T_2) = a + b \log\ k(\text{at } T_1) \tag{4}$$

In the present study linear plots imply the validity of isokinetic relationship. The linear relationship in Exner plots (Exner, 1964; Exner et al., 1973) at $4 + \log k_2$ (298 K) and $4 + \log k_2$ (308 K) observed is shown in Fig. 3 (slope = 0.94, $r^2 = 0.992$, isokinetic temperature = 685 K). The operation of isokinetic relationship reveals that a single mechanism is operating in all the mole fractions of the solvent (Leffler and Grunwald, 1963).

3.5. Solvent–reactivity correlation

The influence of solvent on the rate of oxidation of methionine by BIFC was studied in water–acetic acid mixtures with ten different mole fractions of the organic co-solvent *viz*. acetic acid. The results in Table 3 indicate that the reaction constant k_2 is remarkably sensitive to the composition of the mixed solvent. The rate constant increases with increasing mole fraction of acetic acid in the mixture.

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

The most celebrated Kamlet–Taft solvatochromic comparision method developed by Kamlet (Kamlet et al., 1983, 1981) has been used in order to obtain a deeper insight into the various solute–solvent interactions. 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:

$$\log\ k_2 = A_o + s\pi^* + b\beta + a\alpha \tag{5}$$

where π^* is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, α is the solvent hydrogen bond donor (HBD) acidity, β is the solvent hydrogen bond acceptor (HBA) basicity and A_o is the intercept term.

In order to explain the kinetic results through the solvent polarity and basicity or acidity, the rate constants were correlated with he solvatochromic parameters π^*, α and β using total solvatochromic equation, Eq. (5). The correlation of kinetic data was realized by means of multiple linear regression analysis.

The regression coefficients *s, a* and *b* measure the relative susceptibilities of the solvent dependent solute property $\log k_2$ to the indicated solvent parameter. The rate of oxidation in the studied solvent mixtures shows good correlations with solvent via the above LSER. The correlation results obtained are as follows:

$$\log\ k_2 = -9.23(\pm 2.31) - 2.46(\pm 0.12)\pi^* + 4.83(\pm 1.08)\alpha + 7.23(\pm 2.87)\beta$$

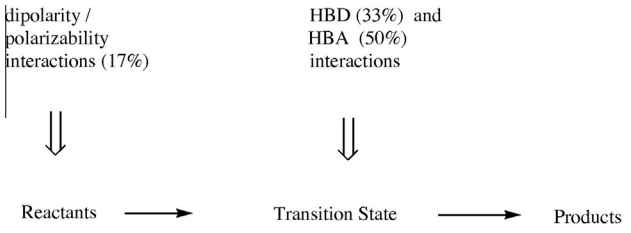
$$(N = 10, \quad r^2 = 0.983, \quad sd = 0.04, \psi = 0.10, \quad P_\alpha = 33\%, \quad P_\beta = 50\%, \quad P_{\pi^*} = 17\%)$$

Such a good correlation, with an explained variance of *ca.* 98% in the water–acetic acid mixtures, indicate the existence of non-specific and specific solvent–solute interactions. From the values of the regression coefficients, the contribution of each parameter (P_x), on the percentage basis, to the reactivity were calculated (Fathima Jeyanthi and Elango, 2003; Saravanakumar and Elango, 2002).

The systematic multiple regression analysis leads to the following conclusions (Pandeeswaran et al., 2005)

(i) In water–acetic acid mixtures, the rate of the reaction is strongly influenced by specific solute–solvent interaction, as indicated by the percentage contribution of the parameters α and β.
(ii) The positive signs of the coefficients of the α and β terms suggests that the specific interaction between the transition state and the solvent, through hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) properties, are greater than those between the reactants and the solvent.
(iii) The contribution of the solvent HBA basicity, β, to the total solvent effect is the predominant. The positive sign of the coefficient of this term suggests that the solvent mixture solvates the transition state more than the reactants. Since acetic acid is an amphiprotic solvent, increasing its mole fraction in the solvent mixture stabilizes the transition state through better solvation and consequently increases the rate of oxidation.
(iv) The solvent dipolarity/polarizability π^* plays a very minor role. The negative sign of the coefficient of this term suggests that the reactants are solvated to a greater extent by the solvent mixture than in the transition state.

Considering these points, the solvation model for the oxidation of methionine by BIFC in water–acetic acid mixtures can be prepared as:



3.6. Mechanism of oxidation

Based on the above kinetic observations, *i.e.* first order dependence on [Met], [BIFC] and [H^+], the following mechanism is proposed. The insignificant variations with ionic strength may be attributed to the absence of ion–ion interactions in the rate determining step. The rate constants increase significantly with increasing the acetic acid content of the solvent, suggesting a facile reactivity in a medium of low dielectric constant. In general, such rate enhancements in a less polar solvent are ascribed to the facility of formation of Cr(VI) ester (Westheimer, 1949; Meenashisundaram and Sockalingam, 2001). Quite likely, the formation of chromate ester in the present study is favoured in the medium of low permittivity. Under the present experimental conditions, methionine is oxidized to the sulfoxide stage only. The linear increase in the rate with acidity suggests the involvement of protonated BIFC in the rate determining step. In the first step BIFC becomes protonated. The protonated BIFC attacks the substrate, in a slow step, to form a complex, which subsequently decomposes to give the products in a fast step. The proposed scheme envisages an oxygen atom transfer from the oxidant and that is in agreement with the earlier observations. The electrophile attack on the sulfide–sulfur can be viewed as a S_N2 reaction (Pandeeswaran et al., 2005).

The above mechanism leads to the following rate law:

$$\text{Rate} = K\,[\text{Complex}]$$
$$[\text{Complex}] = K'\,[\text{Met}]\,[\text{BIFCH}^+]$$
$$[\text{BIFCH}^+] = k[\text{BIFC}][\text{H}^+]$$
$$[\text{Complex}] = KK'k[\text{Met}][\text{BIFC}][\text{H}^+]$$
$$-\text{d}[\text{BIFC}]/\text{dt} = KK'k\,[\text{Met}]\,[\text{BIFC}]\,[\text{H}^+]$$

The rate law in its final form accounts for the observed kinetics. The negative entropy of activation suggests complex formation in the transition state.

4. Conclusion

The oxidation of methionine by BIFC is first order with respect to [Met], [BIFC] and [H^+]. Methionine is oxidized to sulfoxide stage only. The entropy of activation is negative, suggesting the formation of a complex in a rate-determining step. The solvent effect has been analysed using the Kamlet multi parametric equation. The significance of the various solute–solvent interactions has been established using the multiple regression analysis.

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