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Kinetics and mechanism of oxidation of DL-methionine by hexacyanoferrate(III) in aqueous alkaline medium

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The title reaction was studied spectrophotometrically. The reaction was found to be first order in [HCF] and fractional order each in [DL-methionine] and [OH^-]. Initially added products did not alter the rate of reaction. The variation of ionic strength had unaltered the rate of reaction whereas dielectric constant of the medium had an influence on k_{obs} values. A suitable mechanism was proposed in which oxidant was involved in the formation of adduct (K_2) which is formed by reacting with DL-methionine in a prior equilibrium step. It decomposes in a slow step (k) to form a free radical generated on DL-methionine. This free radical leads to methionine sulfoxide in the fast step by reacting with another molecule of hexacyanoferrate(III). The effect of temperature on rate of reaction was also studied. Activation parameters were evaluated. The rate law was derived as:

$$k_{obs} = \frac{kK_1K_2[\text{DL-methionine}][OH^-]}{1 + K_1[OH^-] + K_2[\text{DL-methionine}] + K_1K_2[\text{DL-methionine}][OH^-]}.$$

The reaction constants are calculated.

Keywords: kinetics; oxidation; DL-methionine; hexacyanoferrate(III); mechanism

1. Introduction

Hexacyanoferrate(III), HCF is a stable octahedral complex anion. It is a mild oxidizing agent as it has the moderate (*1*) reduction potential (0.41 V). It is mainly used (*1*) as an oxidizing agent in the oxidation of variety of organic compounds (oxygenated, sulfated, nitrogenated, unsaturated, etc.). Recently Leal *et al.* (*2*) have reviewed the oxidation studies of hexacyanoferrate(III). It reveals that the order in oxidant and reductant is found to be one each in uncatalyzed reactions, whereas in Ru(III) catalysis, the rate was found (*3, 4*) to be independent of [HCF]. It also emphasizes that HCF exists as an ion pair form by pairing with Na^+ or K^+ present in the reaction mixture.

DL-Methionine (DL-M) is a sulfur-containing essential α-amino acid which is not synthesized in the body and must be supplemented through the food. It contributes to supply mineral sulfur improving tone and pliability of the skin, conditioning the hair and strengthening nails, and protecting the cells from airborne pollutants. It contributes to other compounds including *S*-adenosyl methionine (SAM), which transfer the active labile methyl group and mineral sulfur to over 100

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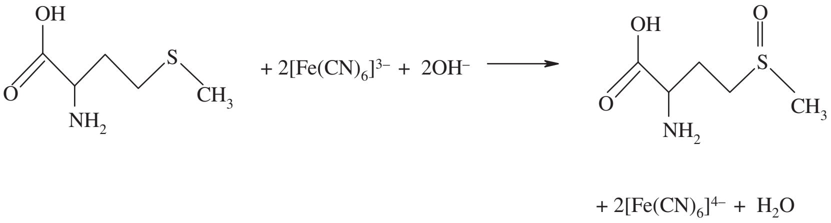
biochemical reactions for normal brain function, and L-cystine, which is a component of glutathione, an important antioxidant molecule in the body. The active transfer of the methyl group is due to the interaction of adenosine triphosphate and a liver enzyme such as phosphatase or dehydrogenase, with a high-energy *S*-methyl bond.

It is known that DL-methionine has three coordinating canters *viz.* O, N and S. Its oxidation path is well established (*5–9*) with various oxidants. In all such cases (*10–12*) it is reported that, 'S' moiety is more susceptible for oxidation. However, the other α-amino acids such as L-histidine, phenyl alanine, leucine, glycine and valine are oxidized (*13*, *14*) by HCF to yield keto acids and ammonia. In case (*15*) of oxidation of D-proline and L-methionine by Mn(III) (*16*) and HCF catalyzed by Os(VIII) (*17*), the products and other kinetic results are found to be substantially different from the present investigation. Apart from this and the fact that in the present investigation the added ferrocyanide did not alter the rate of reaction which is uncommon feature in ferricyanide oxidations. Hence, the title study is undertaken to establish the oxidation path of DL-methionine by HCF in an aqueous alkaline medium.

2. Results

2.1. *Stoichiometry*

Ten different sets of concentrations of DL-methionine and HCF were kept at constant [OH^-] and ionic strength in an inert atmosphere at 28°C for over 48 h in a closed vessel. The remaining HCF was estimated spectrophotometrically by measuring the absorbance at 420 nm. The results indicated that two moles of HCF were consumed by one mole of DL-methionine as in Equation (1).



(1)

The oxidation product of DL-methionine was found to be methionine sulfoxide, which was characterized by the spot test (*18*) and also confirmed as described below. After completion of the reaction, the sodium carbonate was added with vigorous stirring along with drop wise addition of benzyl chloride solution to give a precipitate of *N*-benzoyl methionine sulfoxide, whose identity was confirmed (*19*) by its melting point (183°C). The product, methionine sulfoxide, was precipitated by adding an acetone–ethanol mixture of 1:1 volume ratio to the reaction solution previously brought to pH 4.0. It was subjected to IR analysis. It had shown a strong absorption at 1045 cm^{-1}, in addition to the normal characteristic bands of the ionized carboxylic group and of an amine salt occurring between 3130 and 2500 cm^{-1}. The appearance of a band at 1045 cm^{-1} indicates that DL-methionine is oxidized to sulfoxide without affecting any other part of the carbon chain leading to the formation of keto acid or aldehyde.

2.2. *Effect of varying oxidant concentration*

The effect of [HCF] on the reaction rate was studied by varying the [HCF] from 7.0×10^{-5} to 7.0×10^{-4} mol dm^{-3} at constant concentrations of DL-methionine, alkali and ionic strength and temperature (Table 1). It was observed that the slope of the plot of log (conc.) versus time

Table 1. Effect of variation of [HCF], [DL-M] and [OH^-] on the oxidation of DL-methionine by hexacyanoferrate(III) in aqueous alkaline medium at 28 °C, $I = 1.0\,\text{mol}^{-1}\,\text{dm}^{-3}$.

[HCF] × 10^4 (mol dm^{-3})	[DL-M] ×10^2 (mol dm^{-3})	[OH^-] (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})	$k_{cal} \times 10^{4a}$ (s^{-1})
0.70	4.0	1.0	1.22	1.23
1.0	4.0	1.0	1.20	1.23
2.0	4.0	1.0	1.21	1.23
3.0	4.0	1.0	1.20	1.23
4.0	4.0	1.0	1.22	1.23
5.0	4.0	1.0	1.23	1.23
7.0	4.0	1.0	1.20	1.23
4.0	0.50	1.0	0.411	0.399
4.0	0.80	1.0	0.552	0.551
4.0	1.0	1.0	0.628	0.630
4.0	2.0	1.0	0.917	0.921
4.0	5.0	1.0	1.41	1.42
4.0	7.0	1.0	1.69	1.62
4.0	4.0	0.10	0.340	0.338
4.0	4.0	0.15	0.421	0.416
4.0	4.0	0.20	0.509	0.520
4.0	4.0	0.40	0.722	0.718
4.0	4.0	0.60	0.932	0.934
4.0	4.0	0.80	1.12	1.13

Note: [a]The k_{cal} are calculated by using k, K_1 and K_2 as $2.44 \times 10^{-4}\,s^{-1}$, 2.9 and $55.3\,dm^3\,mol^{-1}$, respectively, in rate law (7).

remained constant for most of the different [HCF] values. It was also confirmed by the linearity of the first-order plot after a small initial period. Hence, the order in [HCF] was considered as unity.

2.3. *Effect of varying substrate concentration*

The DL-methionine was varied in the concentration range from 5.0×10^{-3} to $7.0 \times 10^{-2}\,\text{mol dm}^{-3}$ while the concentrations of all other reactants were held constant. It was observed that the rate constant of reaction was increased with increase in DL-methionine concentration (Table 1). The order of DL-methionine concentration was calculated from the slope of plot of $\log k_{obs}$ versus log [DL-methionine] and found to be 0.5.

2.4. *Effect of alkali concentration*

The effect of OH^- concentration on the reaction rate was studied in the concentration range 0.1–1.0 mol dm^{-3} while the concentrations of all other reactions were held constant. It was noticed that there was an increase in 'k_{obs}' with increasing the concentration of OH^- (Table 1). The slope of the plot of $\log k_{obs}$ versus log[OH^-] lead the order 0.55.

2.5. *Effect of ionic strength and solvent polarity*

The effect of ionic strength was studied by varying [NaCl] in the reaction medium. The ionic strength of the reaction medium was varied from 0.2 to 1.5 mol dm^{-3} at constant [HCF], [DL-methionine] and [OH^-]. It was found that the ionic strength had no influence on the rate of the reaction.

The relative permittivity (D) effect was studied by varying the t-butyl alcohol–water content in the reaction mixture with all other conditions being kept constant. The D values were computed

(*20*) from the values of pure liquids. In the reaction, as '*D*' decreases the k_{obs} values increased. The graph of $\log k_{obs}$ versus $1/D$ was found to be linear with a positive slope. Earlier the reaction between *t*-butyl alcohol and oxidant was studied. It was observed that there was no reaction between solvent and oxidant.

2.6. *Effect of initially added products*

The added products, $[Fe(CN)_6]^{-4}$ and methionine sulfoxide, did not alter the rate of reaction in the studied concentration range of 8.0×10^{-5}–7.0×10^{-4} mol dm^{-3} at constant concentrations of all reactants and conditions.

2.7. *Intervention of free radicals*

The polymerization study reveals that the oxidation of DL-methionine was followed with an intervention of free radicals.

2.8. *Effect of temperature*

Kinetics were also carried out at various temperatures by varying [DL-methionine] at constant concentrations of HCF, OH$^-$ and ionic strength. The rate of reaction increased with increasing temperatures. The values of k_{obs} at different temperatures were tabulated in Table 2. The energy of activation was determined from the slope of the Arrhenius plot of $\log k_{obs}$ versus $1/T$. The other activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$ and $\log A$ were also calculated (Table 3). Apart from this, the equilibrium constants for the adduct formation (discussed in the mechanism) at various temperatures were evaluated from the plot of $1/k_{obs}$ versus 1/[DL-methionine] plot (Figure 1). From Van't Hoff's plot of $\log K$ versus $1/T$, the thermodynamic quantities ΔH, ΔS and ΔG were also calculated for the equilibrium of the adduct formation (see discussion section). Both activation parameters and thermodynamic parameters are tabulated in Table 3.

Table 2. Effect of temperature on rate for the oxidation of DL-methionine by hexacyanoferrate(III) in aqueous alkali and equilibrium constant of adduct. $[HCF] = 4.0 \times 10^{-4}$, $[DL\text{-}M] = 4.0 \times 10^{-2}$, $[OH^-] = 1.0$ mol dm^{-3}, $I = 1.0$ mol^{-1} dm^{-3}.

Temperature (K)	$k_{obs} \times 10^4$ (s^{-1})	K_2 (dm^3 mol^{-1})
301	1.21	55.3
306	1.64	64.9
311	2.40	76.9
316	3.41	88.0

Table 3. Thermodynamics and activation parameters for the oxidation of DL-methionine by hexacyanoferrate(III) in aqueous alkaline medium.

Activation parameters	Values	Thermodynamic parameters	Values
E_a (kJ mol^{-1})	55.7 ± 2		
$\Delta H^{\neq}$ (kJ mol^{-1})	53.2 ± 2	ΔH (kJ mol^{-1})	-24 ± 1
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	-42 ± 1	ΔS (J K^{-1} mol^{-1})	$+112 \pm 4$
$\Delta G^{\neq}$ (kJ mol^{-1})	66 ± 2	ΔG (kJ mol^{-1})	-57 ± 2
$\log A$	6.0 ± 0.2		

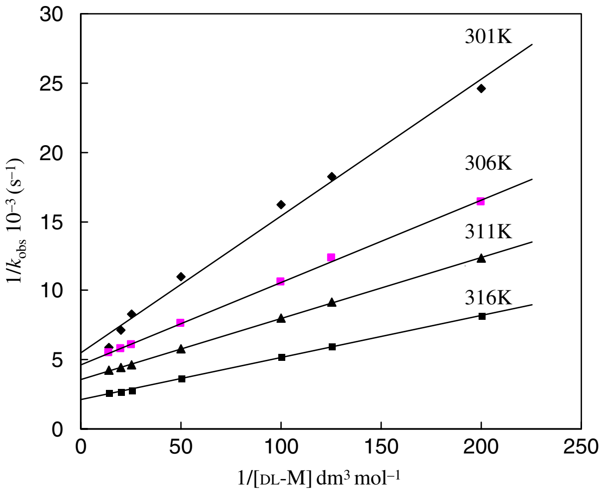
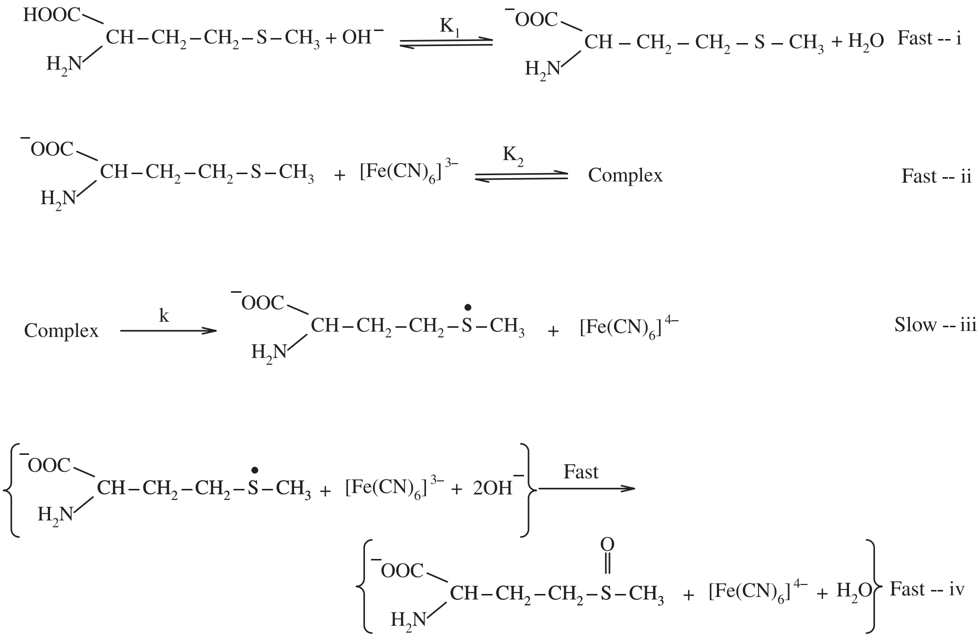


Figure 1. Verification of rate law (7) on the oxidation of DL-methionine by hexacyanoferrate(III) in aqueous alkaline medium for various temperatures at different [DL-methionine].

Each fractional order in $[OH^-]$ and [DL-methionine] is an implicit fact to support the pre-equilibrium before forming the adduct; the adduct is formed by interacting with DL-methionine and HCF in pre-equilibrium before the rate determining step, and the polymerization study strongly supports the free radical intervention generated from the DL-methionine oxidation by alkaline HCF. These results can be accommodated in the mechanism as shown in Scheme 1.



Scheme 1. Mechanism of oxidation of DL-methionine by alkaline hexacyanoferrate(III).

DL-Methionine has three donor atoms namely ‘N’ from amino moiety, ‘O’ from the carboxylic group and ‘S’ of the thionyl group. It is a known fact that ‘N’ and ‘O’ of α-amino acid are involved in coordination with metal ions by donating a pair of electrons. However, in the present study aqueous alkali is used as reaction medium. Hence, their involvement in the adduct formation with HCF can be ruled out. Moreover, the product of DL-methionine is found to be its sulfoxide. Hence, it can be ascertained that sulfur atom donates a pair of electrons to the HCF in the formation of adduct.

It is also known that HCF is an inert complex and exchange of CN^- with DL-methionine is quite unusual as CN^- is a labile ligand. Nevertheless, HCF is reported (*21*, *22*) to be involved in an outer sphere electron exchange with thio compounds by forming intermediate complex of $[Fe(CN)_5\text{–}CNSO_3]^{5-}$ particularly with SO_3^{2-} or $S_2O_3^{2-}$. Lancaster and Murray (*23*) have suggested that many oxidations by transitional metal complex of weak oxidants may proceed *via* intermediate complexes as described in the case of the $[Fe(CN)_6]^{3-}\text{–}SO_3^{2-}$ system. In all such cases, the thio compounds are bonded with one of the CN^- ligands through $CN\text{–}SO_3^{2-}$. This $CN\text{–}SO_3^{2-}$ facilitates the transfer of electron from sulfur to metal ion through the CN group. The analogous complexes in the present study may also be possible as sulfur is present in the α-amino acid. This is evidenced from the plot of log (absorbance) versus time (Figure 2), which is a curve at the initial stage and subsequently of constant slope, *i.e.* the reaction occurs in two consecutive stages (Figure 2). In the first stage of the curve, the outer sphere complex may be rapidly formed between DL-methionine and HCF followed by its oxidation in a linear portion of the second stage as shown in Figure 2.

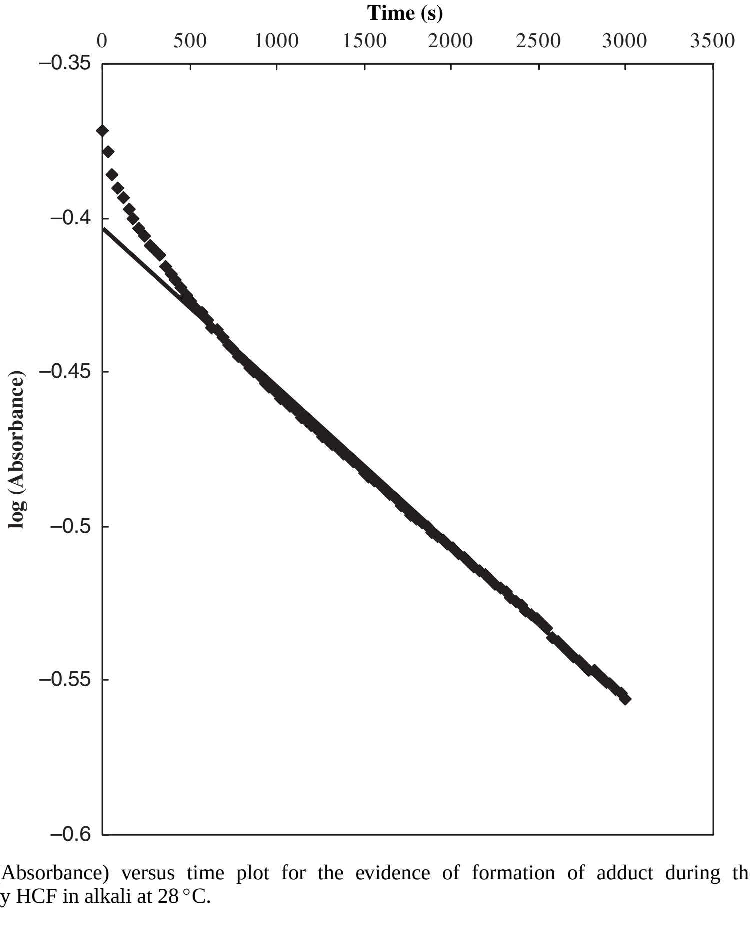
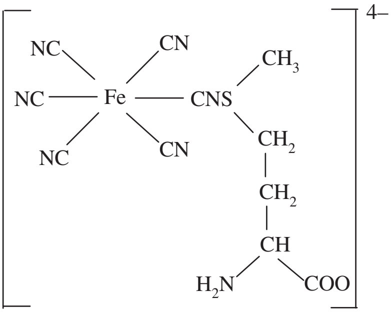


Figure 2. log (Absorbance) versus time plot for the evidence of formation of adduct during the oxidation of DL-methionine by HCF in alkali at 28 °C.

A similar adduct formation between DL-methionine and *cis*-diaquaethylenediamineplatinum(II) perchlorate has been reported (*7*). The probable structure of the adduct can be represented as



The mechanism as written in Scheme 1 suggests that the oxidation takes place when the adduct is decomposed by giving free radicals generated from –S– as HCF is a single equivalent oxidant. The polymerization study also envisages the formation of free radicals. In the subsequent fast step, this free radical is further oxidized by reacting with another molecule of HCF to yield sulfoxide in the fast step. The rate law for the above mechanism can be derived as

$$-\frac{\mathrm{d[HCF]}}{\mathrm{d}t} = k[\text{complex}]$$

$$\text{Rate} = kK_1K_2[\text{Fe(CN}_6)]^{3-}[\text{DL-methionine}]_f[\text{OH}^-]. \quad (2)$$

However,

$$\begin{aligned}[\text{Fe(CN)}_6]^{3-}_T &= [\text{Fe(CN)}_6]^{3-}_f + [\text{complex}],\\ &= [\text{Fe(CN)}_6]^{3-}_f[\text{K}_2(\text{CN})_6]^{3-}_f[\text{DL-methionine}]^-_f,\\ &= [\text{Fe(CN)}_6]^{3-}_f\{1+K_2\}[\text{DL-methionine}]^-_f,\end{aligned}$$

$$[\text{Fe(CN)}_6]^{3-}_f = \frac{[\text{Fe(CN)}_6]^{3-}_T}{1+K_2[\text{DL-methionine}]^-_f}. \quad (3)$$

From the equilibrium (i), the $[\text{OH}^-]_f$ can be given as

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]_T}{1+K_1[\text{DL-methionine}]_f}. \quad (4)$$

In view of low concentration of DL-methionine used in the present study the term K_1[DL-methionine]$_f$ is negligibly small compared with ‘1’ in the denominator of Equation (4). Hence, the denominator tends to unity.

Similarly,

$$\therefore [\text{OH}^-]_f = [\text{OH}^-]_T$$

$$[\text{DL-Methionine}]_T = [\text{DL-methionine}]_f + [\text{DL-methionine}]^- + [\text{complex}].$$

The [DL-methinonine]$_f$ can be calculated from the equilibria (i) and (ii):

$$[\text{DL-Methionine}]_f = \frac{[\text{DL-methionine}]_T}{1+K_1[\text{OH}^-]_f + K_1K_2[\text{Fe(CN)}_6]^{3-}_f[\text{OH}^-]_f}.$$

In view of the low $[\text{Fe(CN)}_6]^{3-}$ used in the experiment, the term K_1K_2 $[\text{Fe(CN)}_6]^{3-}$ $[\text{OH}^-]$ in the denominator of RHS can be neglected.

Thus,

$$[\textsc{dl}\text{-Methionine}]_f = \frac{[\textsc{dl}\text{-methionine}]_T}{1 + K_1[\mathrm{OH}^-]_f}. \tag{5}$$

On substituting Equations (3)–(5) in Equation (2), the following equation results:

$$\text{Rate} = \frac{kK_1K_2[\mathrm{Fe(CN)_6}]_T^{3-}[\textsc{dl}\text{-methionine}]_T[\mathrm{OH}^-]_T}{1 + K_1[\mathrm{OH}^-]K_2[\textsc{dl}\text{-methionine}] + K_1K_2[\textsc{dl}\text{-methionine}][\mathrm{OH}^-]},$$

$$k_{\mathrm{obs}} = \frac{kK_1K_2[\textsc{dl}\text{-methionine}]_T[\mathrm{OH}^-]_T}{1 + K_1[\mathrm{OH}^-]_f + K_2[\textsc{dl}\text{-methionine}]_f + K_1K_2[\textsc{dl}\text{-methionine}]_f[\mathrm{OH}^-]_f}. \tag{6}$$

For the verification of rate law, the subscripts 'T' and 'f' are omitted and hence, Equation (6) becomes

$$k_{\mathrm{obs}} = \frac{kK_1K_2[\textsc{dl}\text{-methionine}]_T[\mathrm{OH}^-]}{1 + K_1[\mathrm{OH}^-] + K_2[\textsc{dl}\text{-methionine}] + K_1K_2[\textsc{dl}\text{-methionine}][\mathrm{OH}^-]}. \tag{7}$$

Equation (7) is rearranged into Equation (8),

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{kK_1K_2[\textsc{dl}\text{-methionine}][\mathrm{OH}^-]} + \frac{1}{kK_2[\textsc{dl}\text{-methionine}]} + \frac{1}{kK_1[\mathrm{OH}^-]} + \frac{1}{k}. \tag{8}$$

The mechanism as in Scheme 1 and rate law (7) are verified in the form of Equation (8) by plotting the graphs of $1/k_{\mathrm{obs}}$ versus $1/[\mathrm{OH}^-]$ and $1/[\textsc{dl}\text{-M}]$. They should be linear and found so in Figures 1 and 3. From the slopes and intercepts of such plots, the values of k, K_1 and K_2 are calculated as $2.44 \times 10^{-4}\,\mathrm{s}^{-1}$, 2.9 and $55.3\,\mathrm{dm}^3\,\mathrm{mol}^{-1}$, respectively, for 28° C. Further, these values are used in rate law (7) at different experimental conditions as in Table 1 to regenerate k_{obs}. The regenerated values are found to be in close agreement with those of experimentally observed values. This fortifies the mechanism and rate law (7).

The outer sphere mechanism of oxidation of DL-methionine by HCF is evidenced by the large value of energy of activation $55.7\,\mathrm{kJ\,mol}^{-1}$. This outer sphere complex may be more ordered than its reactants as it is evidenced by the negative value of $\Delta S^{\neq}$ ($-42\,\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$). However, the independency of k_{obs} on ionic strength variation cannot be accounted. This may be due to the direct interaction of the CN group of HCF with 'S' of DL-methionine, otherwise, there would be an ionic strength effect on rate of reaction. This direct interaction between CN and 'S' is also evident from the relatively small value of log A (6.0).

An increase in rate with decrease in the dielectric constant of the medium is contradictory to the expected direction (*24*) as ionic species are involved in the prior equilibrium step of the slow step as shown in Scheme 1. This may be due to more solvation of the activated complex at low dielectric constant of the reaction media rather than that of a higher one where the reactants are more solvated.

The [DL-methionine] was varied at four different temperatures at constant concentrations of oxidant, OH^- and ionic strength, and from the slopes and intercepts of plot of $1/k_{\mathrm{obs}}$ versus 1/[DL-methionine], the K_2 values were determined for all the temperatures varied and used to plot Van't Hoff's graph (*i.e.* $\log K_2$ versus $1/T$). From the slopes and intercept of such plots, the thermodynamic quantities like enthalpy change (ΔH) of the second equilibrium step (K_2) of the reaction, entropy of the reaction (ΔS) and free energy of the reaction (ΔG) were calculated (Table 3). These values are compared with the values obtained for the slow step of the reaction and show that the adduct forms fairly fast ($\Delta G = -57\,\mathrm{kJ\,mol}^{-1}$); and it can be concluded that the adduct formation is thermodynamically controlled rather than the kinetics. The ΔH, $-24\,\mathrm{kJ\,mol}^{-1}$ indicates that the adduct formation is exothermic and highly reactive as evidenced by the large positive value of ΔS ($+112\,\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$).

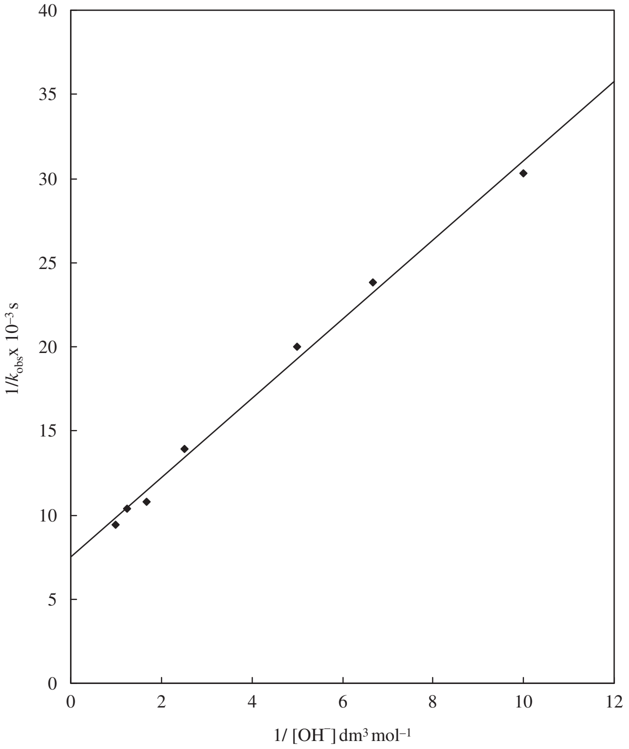


Figure 3. Verification of rate law (7) for the oxidation of DL-methionine by hexacyanoferrate(III) in aqueous alkali at 28 °C.

3. Conclusion

The mechanism of oxidation of DL-methionine by alkaline HCF was proposed as an outer-sphere election transfer through an infused ligand of CN and S of DL-methionine. The complex formation was evidenced by the rapid fall of absorbance of HCF in the presence of DL-methionine at the initial stage of the reaction (Figure 2).

The oxidation product of DL-methionine was identified as methionine sulfoxide which is unlike the formation of L-methionine from D-methionine in the metabolism via the formation of keto-acid followed by re-amination. The thermodynamic parameters of formation of adduct between HCF and DL-methionine was found to be thermodynamically controlled as evidenced by the large negative value of ΔG ($-57\,\mathrm{kJ\,mol^{-1}}$). However, this adduct may be relatively less active compared with the adduct formed (*17*) between HCF and Os(VIII) in the oxidation of DL-methionine by Os(VIII) catalyzed HCF in alkali in which the reaction occurred 1,20,000 times faster than the uncatalyzed one even in the lower concentration of DL-methionine.

4. Experimental

All chemicals used were of reagent grade. Millipore water was used throughout the study. An aqueous solution of HCF was prepared by dissolving $K_3[Fe(CN)_6]$ (BDH) in water and was standardized (*25*) iodometrically. DL-methionine, a colorless crystalline compound (E-Merck), was used without further purification for the preparation of aqueous stock solution. Aqueous solutions of $K_4[Fe(CN)_6]$ and DL-methionine sulfoxide were used to study the effect of products on the rate of reaction. Aqueous solutions of NaOH and NaCl were used to maintain the $[OH^-]$ and ionic strength, respectively.

4.1. *Kinetics measurements*

The reaction was initiated by mixing HCF solution with DL-methionine which also contained the required amounts of NaOH and NaCl to maintain constant concentration of alkali and ionic strength, respectively. The progress of the reaction was monitored by measuring the absorbance of HCF using a Hitachi U-3010 spectrophotometer (Tokyo, Japan) at its absorption maximum $\lambda_{max} = 420$ nm in which all other species in the reaction medium at this wave length were found to have negligible interferences. Earlier, the obedience of HCF to Beer's law at 420 nm was studied in the concentration range, 5.0×10^{-5}–8.0×10^{-4} mol dm^{-3} and the molar extinction coefficient (ε) was found to be 1060 ± 40 dm^3 mol^{-1} cm^{-1}. The pseudo-first order rate constant k_{obs} were calculated from the slopes of log[HCF] versus time plots, which were linear up to 80% completion of the reaction in most of the variations of concentrations of oxidant, reductant and alkali except at the initial stage (Figure 2). Orders with respect to each reactant are determined from the slopes of plots of log k_{obs} versus log(conc.) except in [HCF]. The results were reproducible within ±4%.

4.2. *Polymerization study*

The intervention of free radicals generated during the oxidation of DL-methionine with a single equivalent oxidant, [HCF], was expected. This possibility of intervention of free radicals was tested by adding a free radical scavenger, acrylonitrile, while the reaction was in progress. On diluting the reaction mixture with methyl alcohol after the reaction was complete, a copious precipitate of the polymer resulted, indicating that the oxidation occurred *via* the intervention of a free radical. Earlier, it was ascertained that there was no precipitate formed either with the HCF in alkali, DL-methionine in alkali or with OH^- alone with methyl alcohol.

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