Available online at www.sciencedirect.com
SCIENCE DIRECT®
Coordination Chemistry Reviews 248 (2004) 81–99
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

Micellar effect on the kinetics and mechanism of chromium(VI) oxidation of organic substrates

Asim K. Das*

Department of Chemistry, Visva Bharati University, Santiniketan 731235, India

Received 21 February 2003; accepted 31 October 2003

Contents

Abstract

The present review discusses different possible routes of reduction of Cr(VI) to Cr(III) by several types of organic reducing agents with special emphasis to those occurring in aqueous micellar systems. The micellar media can influence the mechanistic paths of reduction of Cr(VI) to Cr(III). Such studies in micro-heterogeneous systems are important from the standpoint of understanding the mechanism of redox activity and toxicity of Cr(VI). The possible use of suitable surfactants in the two-phase oxidation of organic substances by chromic acid is discussed.

Keywords: Chromium(VI); Oxidation; Kinetics; Catalysis; Surfactants

1. Introduction

The net 3e-reduction of Cr(VI) to Cr(III) may proceed in different possible ways through the formation of different intermediates like Cr(V), Cr(IV) and Cr(II). The mechanistic path of this reduction depends on the nature of the reductants and reaction conditions [1–3]. To correlate all these aspects is quite important to understand the reactivity of Cr(VI). It is believed that the intermediates like Cr(V), Cr(IV) and free-radicals produced during the cellular reduction of Cr(VI) to Cr(III) by the biogenic reducing

* Tel.: +91-3-463-52751x67; fax: +91-3-463-52672.
E-mail address: ak_das3@rediffmail.com (A.K. Das).

0010-8545/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cct.2003.10.012

agents like glutathione and other possible biomolecules like cysteine, ascorbic acid, Vitamin E, etc. are responsible for the Cr-induced toxicity [2,4–13]. Thus studies on the redox activity of different Cr-species and their biochemistry are important [1,2,14–19]. The organized assemblies may have an important effect [20–29] on the rate of electron transfer reactions. The cytoplasmic reduction of Cr(VI) to Cr(III) occurs in micro-heterogeneous systems. In vitro, the micelles are considered to mimic the cellular membranes. The electron transfer processes occurring in the micellar systems may be considered as models to obtain insight into the electron transport process prevailing in biological systems. The studies on the interfacial electron transfer reactions on the micellar surfaces are not only important to understand the reactivity of Cr(VI) in biological systems but also to establish the pathways leading to the reduction of Cr(VI) to Cr(III). Utilization of the surfactants in the reaction media can affect the rates, reaction yield, products, etc. The present review mainly aims to understand the mechanistic pathways of reduction of Cr(VI) occurring in aqueous micellar media.

2. Physicochemical aspects of surfactants

Generally, the surfactants bear diphilic moieties, i.e. hydrophobic and hydrophilic groups. The structures of ionic surfactants may be represented by RX, where R stands for the hydrocarbon chain containing 8–18 carbon atoms present in an alkyl/aromatic moiety or other types of hydrophobic residue and X is an ionic moiety [30,31(a)]. Depending on the nature of charge on X, the surfactants are classified as anion- and cation-active. For the anion-active surfactants, the hydrophilic moiety contains the groups like sulfate, sulfonate, phosphate or carboxylate. The examples are: $CH_3(CH_2)_nOSO_3^-M^+$, $CH_3(CH_2)_nSO_3^-M^+$, $CH_3(CH_2)_nCO_2^-M^+$, etc. (where M^+: Li^+, Na^+, K^+, MMe_4^+, etc., $n = 7$–17). In this group, sodium dodecyl sulfate (SDS) $C_{12}H_{25}OSO_3^-Na^+$ is a representative example. For the cation-active surfactants, the hydrophilic moiety is generally a quaternary ammonium, pyridinium or phosphonium group. The examples are: $CH_3(CH_2)_n{}^+N(CH_3)_3B^-$, $CH_3(CH_2)_n{}^+N(C_5H_5)_3B^-$, etc. (where B^-: Cl^-, Br^-, OH^-, etc.; $n = 7$–17). The representative example is cetyltrimethylammonium bromide (CTAB), $C_{16}H_{33}N^+Me_3Br^-$. The structures of non-ionic surfactants may also be denoted by RX where X (that is electrically neutral) generally represents a polyoxyethylene residue. Polyoxyethylene(23)dodecanol (Brij 35) is a representative example.

When the surfactants as solutes are taken into aqueous solution, due to the hydrophobic interaction, the solute particles have a tendency to aggregate spontaneously to form thermodynamically stable bigger particles of colloidal dimension. Different factors control the supramolecular structure of self-assembly of the surfactant molecules [31(a)–(c)]. At low concentrations, the surfactant molecules behave just like the ordinary solutes, but after attaining a certain concentration they aggregate (the aggregation number denoted by N may vary from 20 to 100 depending on the conditions) to form the micelles and this minimum concentration at which micellization starts is called critical micelle concentration (cmc). The driving force leading to aggregation of surfactant molecules is the hydrophobic interaction among the hydrocarbon chains [31(b)]. Enlargement of micelles leading to separation of the surfactant as a macrophase is prevented by hydration of the hydrophilic moiety, electrostatic repulsion among the micellar head groups of the approaching micelles (in the case of ionic reactants), steric factors and entropy losses. Thus the micelles do not combine to generate a continuous phase but are uniformly distributed in the aqueous medium to generate a micellar pseudo-phase [31(a),(b)]. The inter-conversion between the micelles and surfactant solute molecules is a reversible process that occurs in a few milliseconds. Hence, it is possible to destroy the micelles to produce the original simple solution of surfactants by simple dilution (provided the concentration of surfactant falls below the critical micelle concentration (cmc)).

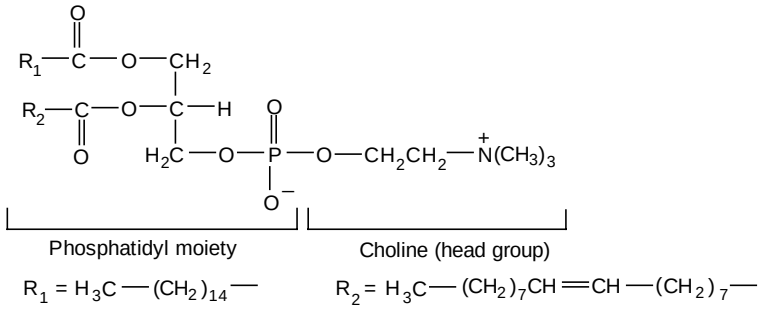
Every surfactant has a definite cmc at a given temperature. The shorter the hydrocarbon chain, the smaller is the decrease in free energy of the micellization process and consequently the higher the cmc. But, the cmc of a particular surfactant is dependent on the chemical composition of the solution in which the micellization is carried out [30,31(a)]. For the ionic surfactants, the factors that minimise the electrostatic repulsion among the hydrophilic moieties (i.e. micellar head groups) favor micellization. The gegenions being oppositely charged are attracted by the micellar head groups and the charge is neutralised. Thus increase in the concentration of gegenions reduces the cmc values [30]. For the non-ionic surfactants, micellization is favored by the increase of temperature that disfavors the hydration of their hydrophilic groups. Micellization occurs in a narrow range of surfactant concentration around the cmc at which there is a sharp change in several properties of the solution (e.g. viscosity, electrical conductivity, surface tension, light scattering, etc.) that indicates the formation of micelles [31(a)]. The aqueous micelles have different forms (e.g. spherical, rod-like, etc.) [31(a),(d),(e)], but all have a common property, the hydrophilic groups projecting outward in contact with the bulk solvent water and the hydrocarbon ends projecting towards the interior side to produce a hydrophobic core. This is why, the aqueous micelles may be simply described as oil in water (o/w, oil represents the non-polar hydrophobic core).

The ionic head groups of ionic surfactants and some of the gegenions form the Stern layer, in which 60–70% of the micellar charge is neutralised. The remaining gegenions form a diffuse Gouy-Chapman layer [30]. Thus to neutralise the charge of the micellar head groups, the counterions are attracted to form electrical double layers. The hydrophobic core of aqueous micelle is closely similar to a liquid hydrocarbon. Thus the hydrophobic core of micelles is suitable to extract the non-polar and hydrophobic substrates from an

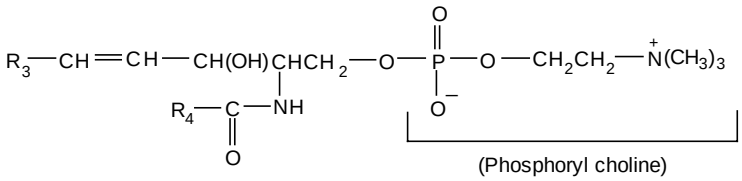
aqueous phase. The non-ionic solutes may be concentrated in the Stern layer but not in the core as it may disrupt the surfactant packing in the micellar core.

The zwitterionic surfactants [31(f)] possessing both the cationic and anionic sites in the polar head groups are biologically and industrially quite important. The betaine surfactants (derived from betaine, $Me_3N^+CH_2CO_2^-$, an oxidation product of choline) are the representative examples (Fig. 1) in this group. The important examples are: lauramidopropyl dimethyl betaine, lauryl dimethyl betaine, cocoamidopropyl dimethyl betaine, etc. These are widely used in industry and cosmetics as foam boosters. These find applications in shampoos, bubble bath, hand soaps, hair conditioners, cleansing lotions and creams. The zwitterionic phospholipid surfactants are involved in constructing the lipid bilayer membranes [31(b),(g),(h)] and lipid vesicles (known as liposomes) [31(g),(i),(j)]. The important zwitterionic phospholipids are: phosphatidyl choline, phosphatidyl ethanolamine, phosphatidyl serine, sphingomyelin (Fig. 1) [31(g),(k),(l)]. In vesicles, an aqueous compartment remains entirely closed by the lipid bilayer membrane composed of phospholipids [31(g)]. The vesicles can be prepared by suspending a suitable phospholipid (e.g. phosphatidyl choline) in an aqueous medium followed by sonication. The vesicles may fuse with the cell membrane to allow the transport of impermeable substances into the cells. This technique involving the selective fusion of lipid vesicles with the specific cells is highly promising to control the delivery of drugs into the target cells [31(g),(m),(n)].

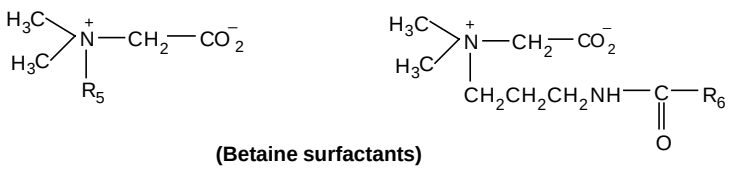
The reverse micelles (water in oil, w/o) represent the oil–surfactant–water ternary systems where oil simply represents the non-polar hydrocarbon dispersant medium [31(c),32]. In reverse micelles produced in non-polar hydrocarbon solvents, the hydrophobic hydrocarbon portion of the surfactants forms the outer layer in contact with the non-polar solvent while the hydrophilic groups of the surfactants remain projected towards the interior portion. In some cases (as in the case of SDS-reverse micelles in alkanols), the dispersant medium may act as a cosurfactant and as a part of the interface [32(b)]. The properties of reverse micelles largely depend on the ratio, $w_0 = [H_2O]/[\text{surfactant}]$ [32(b),(e)]. Reverse micelles formed by AOT (sodium bis(2-ethylhexyl)sulfosuccinate) are well known [32(d),(e)]. In the case of reverse micelles formed by the ionic surfactants, the structure of water confined within the core is drastically affected because of the charged interior surface. In the water pool (spherical in shape) of the reverse micelles, the hydrophilic reactants are stabilized. In the small aqueous compartment, the solubilized polar substrates are more rigidly bound than the substrates in aqueous media. Thus



(Phosphatidyl choline)



(Sphingomyelin)



(Betaine surfactants)

Fig. 1. Some representative zwitterionic surfactants.

the reverse micelles can strongly influence different types of chemical reactions including the enzymatic reactions [33].

3. Different kinetic models to explain the micellar effects

3.1. Berezin's model

According to the Berezin et al.'s approach [30], a solution above the critical micelle concentration (cmc) may be considered as a two-phase system, consisting of an aqueous phase and a micellar pseudo-phase. The reactants (A and B) may be distributed as shown in Scheme 1.

$$A_W + B_W \xrightarrow{k_W} \text{product} \quad (3.1)$$

$$K_A \uparrow\downarrow \quad K_B \uparrow\downarrow$$

$$A_M + B_M \xrightarrow{k_M} \text{product} \quad (3.2)$$

Scheme 1.

A quantitative rate expression for a bimolecular reaction (Scheme 1) occurring only in aqueous (k_W path) and micellar (k_M path) phase for the reactants A and B is given below:

$$k_{exp} = \frac{\{k_M P_A P_B CV + k_W(1 - CV)\}}{(1 + K_A C)(1 + K_B C)} \quad (3.3)$$

Here, k_{exp} is the observed second-order rate constant in aqueous micellar system; C is the total surfactant concentration (molarity) minus cmc $= [D]_T -$ cmc; some authors have defined $C = ([D]_T - \text{cmc})/N$ where N gives the aggregation number. V is the partial molar volume of the surfactant in the micelle; CV and $(1 - CV)$ stand for the fractions by volume of the micellar phase and aqueous phase, respectively; k_M and k_W are the rate constants for the reaction occurring in the micellar phase and aqueous phase, respectively. The binding constants (K) are related to their partition coefficients (P) as: $K_A = (P_A - 1)V$ and $K_B = (P_B - 1)V$.

For the dilute surfactant solutions, where the volume fraction of the micellar phase is small (i.e. $1 \gg CV$), Eq. (3.3) reduces to

$$k_{exp} = \frac{k_M P_A P_B CV + k_W}{(1 + P_A CV)(1 + P_B CV)} = \frac{k_M P_A P_B CV + k_W}{(1 + K_A C)(1 + K_B C)} \quad (3.4)$$

The above rate equation can be analyzed in different cases depending on the situations [30].

3.2. Menger–Portnoy model

The Menger–Portnoy model [34] considers the partitioning of only one reactant (say A) between the micellar and aqueous phase (Scheme 2).

$$A_W + B \xrightarrow{k_W} \text{product} \quad (3.5)$$

$$K_A \uparrow\downarrow$$

$$A_M + B \xrightarrow{k_M} \text{product} \quad (3.6)$$

Scheme 2.

Scheme 2 leads to the following rate law:

$$k_\Psi = \frac{k_M K_A C + k_W}{1 + K_A C} \quad (3.7)$$

where K_A is the binding constant in terms of the micellized surfactant; k_M and k_W are the first-order rate constants in the micellar and aqueous phase and include the concentration of the other reactant (B) in these pseudo-phases; C is the concentration of the micelle and it has been already defined. Using Berezin's model, the same rate equation may be also obtained from Eq. (3.4) under the conditions, $P_A \gg P_B \approx 1$. For $k_M > k_W$, the reaction rate increases with the increase of C and ultimately it reaches the limiting value k_M. Conversely, for $k_M < k_W$, an increase in C produces a decrease in k_{exp} and k_{exp} tends to attain the limiting value k_M. Eq. (3.7) can be rearranged into the reciprocal form as follows:

$$\frac{1}{k_\Psi - k_W} = \frac{1}{K_A C(k_M - k_W)} + \frac{1}{k_M - k_W} \quad (3.8)$$

or,

$$\frac{k_\Psi - k_W}{k_M - k_\Psi} = K_A C \quad (3.9)$$

Bunton and Cerichelli [35] have pointed out that the treatment of Eq. (3.8) (i.e. plot of $1/(k_\Psi - k_W)$ against $1/C$) is very sensitive to the values of cmc that may be affected by the reaction media. They have suggested that in the case of rate retardation by the surfactant, assuming $k_M \approx 0$, modified Eq. (3.11) gives the better estimation of the binding constant K_A.

$$k_\Psi \approx \frac{k_W}{1 + K_A C} \quad (3.10)$$

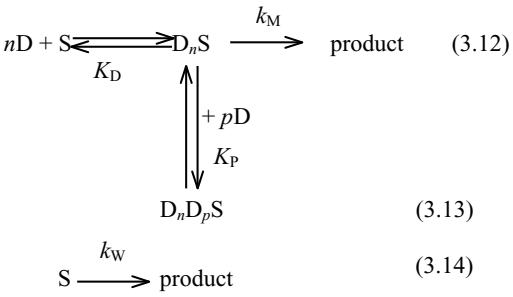
or,

$$\frac{1}{k_\Psi} = \frac{1}{k_W} + \frac{K_A C}{k_W} \quad (3.11)$$

3.3. Cooperative model

The micelle catalyzed reactions may be compared with the enzyme catalyzed reactions. Very often, for the micelle catalyzed reactions, the plot of rate constants versus surfactant concentration gives the sigmoid shaped curves and this observation is analogous to the positive cooperativity (measured by Hill constant n) in the enzymatic reactions. Considering this fact, a kinetic model (Scheme 3) analogous to the Hill model was developed by Piszkiewicz to explain the micellar effect [36]. It considers that the substrate (S) and

detergent (D) molecules aggregate to form the active micelle (D_nS). Very often, in the micelle catalyzed reaction, after attaining a rate maximum, the rate decreases at the higher concentrations of the detergent. To explain the rate retarding effect of the detergent at its higher concentrations, formation of the kinetically inactive micelle (D_nD_pS) through the further aggregation of surfactant molecules has been considered [36]. This phenomenon has been compared with the substrate inhibition in an enzymatic reaction.



Scheme 3.

The second-order rate constant (k_2) for a bimolecular reaction is obtained from the above Scheme as follows.

$$k_2 = \frac{k_M[D]^n + k_W K_D}{K_D + [D]^n + K_P[D]^n[D]^p} \quad (3.15)$$

k_M was taken as the maximum rate constant in the rate constant versus surfactant concentration profile. At the low detergent concentrations, Eq. (3.15) reduces to Eqs. (3.16) and (3.17).

$$k_{obs} = \frac{k_M[D]^n + k_W K_D}{K_D + [D]^n} \quad (3.16)$$

or,

$$\log\left[\frac{k_{obs} - k_W}{k_M - k_{obs}}\right] = \log G = n\log[D] - \log K_D \quad (3.17)$$

At the higher detergent concentrations, Eq. (3.15) reduces to

$$k_2 = \frac{k_M}{1 + K_P[D]^p} \quad (3.18)$$

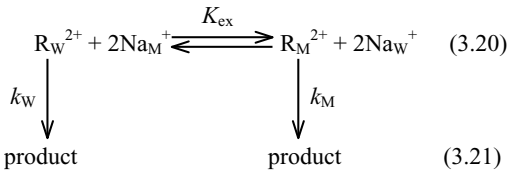
or,

$$\log\left[\frac{k_M}{k_2} - 1\right] = \log K_P + p\log[D] \quad (3.19)$$

To explain the micellar catalysis by Eq. (3.17), it was used in the concentration range in which the initial sigmoid dependence of the rate constant on the detergent concentration was noticed. Thus, though the analysis does not require the knowledge of cmc values of the surfactant, it can be used only at very low concentrations of the surfactant. Eq. (3.17) has been used by many workers [37–39] in the cases where the surfactant shows a monotonic rate retarding effect. On the other hand, Eq. (3.19) is only applicable at the high concentrations of surfactant.

3.4. Pseudo-phase ion-exchange model

In the pseudo-phase ion-exchange (PIE) model [32(a),40], the micellar surfaces are treated as selective ion-exchangers saturated with the counterions. For example, if the reactant is a dipositive species (say R^{2+}) then in the presence of sodium dodecylsulfate (SDS) micelles, both the R^{2+} and Na^+ ions will compete for micellar binding and the pseudo-phase ion-exchange equilibrium will be established (Scheme 4). The equilibrium will be shifted in the direction favoring an increase in the number of reactant species in the aqueous phase with increasing $[Na^+]$.



Scheme 4.

In this model, the ion-specificity for binding has not been considered. If there is a significant ion-specific interaction, then this model will not be applicable. Sometimes, binding of the counterions may perturb the micellar structure and then also the simple ion-exchange model will not be applicable.

For the H^+-catalyzed reaction in the anionic (SDS) micellar pseudo-phase, the following exchange equilibrium between the H^+ ion and Na^+ ion at the micellar surface is very important. Here, there is no specific interaction with the micellar head group for the H^+ ion and Na^+ ion [32(a)].

$$H_W{}^+ + Na_M{}^+ \rightleftarrows H_M{}^+ + Na_W{}^+ \quad (3.22)$$

The ion-exchange equilibrium constant (K_{ex}^H) is defined as

$$K_{ex}^H = \frac{[H_M{}^+][Na_W{}^+]}{[H_W{}^+][Na_M{}^+]} \quad (3.23)$$

where the subscripts M and W denote the micellar and aqueous phase, respectively. The concentrations are expressed in terms of the total solution volume and it is further assumed that the activity coefficient ratios, $\gamma_M(Na^+)/\gamma_M(H^+)$ and $\gamma_W(Na^+)/\gamma_W(H^+)$ are each equal to unity. Considering the competition between the Na^+ ion and H^+ ion only, the overall micellar binding parameter is given by

$$\beta = m_H + m_{Na} = \frac{[H_M{}^+]}{[D_n]} + \frac{[Na_M{}^+]}{[D_n]} = \frac{[H_M{}^+] + [Na_M{}^+]}{[D_n]} \quad (3.24)$$

Thus, β gives the fraction of micellar head groups neutralised. Here $[D_n]$ gives the micellized surfactant concentration, i.e. $[D_n] = [SDS]_T - cmc$. The various concentration terms are expressed as

$$[H_M{}^+] = m_H[D_n],$$

$$[H_W{}^+] = [H^+]_T - [H_M{}^+] = [H^+]_T - m_H[D_n],$$

$$[Na_W{}^+] = [Na^+]_T - [Na_M{}^+] = [Na^+]_T - (\beta - m_H)[D_n];$$

$$[Na_M{}^+] = [Na^+]_T - [Na_W{}^+] = (\beta - m_H)[D_n]$$

The ion-exchange equilibrium constant can be expressed as

$$K_{ex}^{H} = \frac{m_H\{[Na^+]_T - (\beta - m_H)[D_n]\}}{(\beta - m_H)([H^+]_T - m_H[D_n])} \quad (3.25)$$

The Eq. (3.25) on rearrangement yields

$$(m_H)^2(K_{ex}^{H} - 1)[D_n] - m_H\{K_{ex}^{H}[H^+]_T + [Na^+]_T + \beta[D_n](K_{ex}^{H} - 1)\} + K_{ex}^{H}\beta[H^+]_T = 0 \quad (3.26)$$

Thus $[H_M{}^+]$ $(=m_H[D_n])$ can be calculated by using Eq. (3.26). For the H^+ ion, K_{ex}^{H} is close to unity [32(a)]. This indicates that there is no specific interaction for the H^+ ion or Na^+ ion with the micellar surface and consequently these ions are statistically distributed between the aqueous and micellar phases. If $K_{ex}^{H} \to 1$, then Eq. (3.25) leads to

$$[H_M{}^+] = \frac{[H^+]_T\beta[D_n]}{[H^+]_T + [Na^+]_T} \quad (3.27)$$

The value of β has been found to be in the range 0.6–0.85 from the conductivity measurements [32(a)]. It is evident that $[H_M{}^+]$ increases with the increase of $[D_n]$.

3.5. Effect of electrolyte on micelles and micellar kinetics

The surface potential of the ionic micelles decreases with the increase of concentration of the gegenions. This reduces the cmc and it can also change the shape and size of the micelles [30,31(d),(e)]. These effects are more pronounced for the counterions of higher charge and hydrophobicity. Very often, the micellar catalysis in bimolecular reactions is retarded by the addition of electrolytes [35]. This rate retarding effect largely depends on the nature of the counterions. The counterions from the added electrolytes compete with the reactive counterions for micellar binding. This rate retarding effect generally increases with the increase of hydrophobicity of the added counterions. This hydrophobicity favors the micellar binding of the counterions. The higher valent ions are also found more efficient in reducing the micellar catalysis. Sometimes, in the plot of rate versus concentration of the added counterions, there is a minimum followed by a rate enhancement. This generally happens when the counterions are highly hydrophobic. The binding of such hydrophobic counterions can modify the micellar surface that may favor the reaction. The inhibition of micellar catalysis by the added electrolytes may also be interpreted by considering the change of size of the micelles in the presence of salts. The presence of salts increases the aggregation number (and consequently the shape and size) of the micelles [31(d),(e)]. An increase in aggregation number will reduce the number of micelles and as a result, the catalytic efficiency of the detergents decreases.

4. The common pathways leading to reduction of chromium(VI) to chromium(III)

The reduction of Cr(VI) by the one equivalent reductants of transition metal ions like Fe(II), Cr(II), etc. occurs via three consecutive 1e transfer steps, i.e. Cr(VI) → Cr(V) → Cr(IV) → Cr(III) [41]. The two-equivalent inorganic reductants like Sn(II), In(I), Ge(II) reduce Cr(VI) in successive 2e-transfer steps via oxygen atom transfer as follows [42] (Scheme 5).

$$Cr(VI) \xrightarrow[(slow)]{Ge(II)} Cr(IV) \xrightarrow[(rapid)]{Ge(II)} Cr(II) \xrightarrow[(rapid)]{Cr(VI)} Cr(III) + Cr(V) \quad (4.1)$$

$$Cr(V) + Ge(II) \longrightarrow Cr(III) + Ge(IV) \quad (4.2)$$

Scheme 5.

A similar mechanism has been proposed by Perez-Benito and co-workers [43,44] for the Cr(VI) oxidation of different organic substrates where Cr(IV) is reduced to Cr(II) through a hydride transfer pathway. In the presence of a Co(III) complex such as $[(NH_3)_5CoF]^{2+}$, Cr(II) can be trapped in the following reaction [42,45].

$$Cr(II) + Co(III) \to Cr(III) + Co(II), \quad \text{inner-sphere process} \quad (4.3)$$

In the presence of strict two-equivalent inorganic reductants like Sn(II), In(I), Ge(II), As(III), etc. [42,46–48], the Cr(IV) species produced at the rate determining step (rds) can be stabilized by using chelating agents such as ehba (2-ethyl-2-hydroxybutanoate), hmba (2-hydroxy-2-methylbutanoate), (−)quinate [(1*R*,3*R*,4*R*,5*R*)-1,3,4,5-tetrahydroxycyclo hexanecarboxylate] and in fact, the Cr(IV)–ehba complex has been prepared and characterized [46,47]. The structure of Cr(IV)–ehba complex has been determined by X-ray absorption spectroscopic studies [46(b)]. The redox activity of Cr(IV)-species in strongly acidic media has been well studied [15,19(a)].

In the reduction of organic substrates, different possible mechanisms have been proposed depending on the conditions. Watanabe and Westheimer proposed the following mechanism (Scheme 6) [49] for the reduction

$$Cr(VI) + S \rightleftharpoons Cr(VI)\text{–}S, \text{ (complex)} \quad (4.4)$$

$$Cr(VI)\text{–}S \longrightarrow Cr(IV) + P \text{ (Product), (rds)} \quad (4.5)$$

$$Cr(IV) + Cr(VI) \longrightarrow 2\,Cr(V) \quad (4.6)$$

$$Cr(V) + S \longrightarrow P + Cr(III) \quad (4.7)$$

Scheme 6.

of Cr(VI) to Cr(III) by the substrates (S) acting as the two-equivalent reductants. Cr(V) and Cr(IV) are involved as the Cr-intermediates. Here throughout the reaction, different Cr-species act as the 2e-oxidants and this rules out the possibility of free-radical formation.

Though the oxidation of Cr(IV) by Cr(VI) is thermodynamically unfavorable [50(a)] the transient Cr(IV)–aqua

species reacts with Cr(VI) very fast [1]. This is why, reaction 4.6 is quite meaningful and the existence of Cr(IV) and Cr(V) (d^1 system, EPR active) is well established. Scheme 6 has been argued in many cases [1,2,45(b),49,51]. When the Cr(IV)-species is stabilized as in the case of oxidation of oxalic acid by Cr(VI) [52], the reaction (4.6) is questionable. In fact, by considering the thermodynamic unfavorability for the reaction (4.6) and the formation of free-radicals observed in many cases, Rocek suggested a different mechanism (Scheme 7) [50] in which the reductant substrate acts as a two-equivalent reductant towards both Cr(VI) and Cr(V) and as a one equivalent reductant towards Cr(IV).

$$\mathrm{Cr(VI)} + \mathrm{S} \rightleftharpoons \mathrm{Cr(VI)\text{–}S} \quad (4.4)$$

$$\mathrm{Cr(VI)\text{–}S} \longrightarrow \mathrm{Cr(IV)} + \mathrm{P,\ (rds)} \quad (4.5)$$

$$\mathrm{Cr(IV)} + \mathrm{S} \longrightarrow \mathrm{Cr(III)} + \mathrm{R^{\bullet}} \quad (4.8)$$

$$\mathrm{Cr(VI)} + \mathrm{R^{\bullet}} \longrightarrow \mathrm{Cr(V)} + \mathrm{P} \quad (4.9)$$

$$\mathrm{Cr(V)} + \mathrm{S} \longrightarrow \mathrm{Cr(III)} + \mathrm{P} \quad (4.7)$$

Scheme 7.

In both the Westheimer mechanism (Scheme 6) and Rocek mechanism (Scheme 7), there exists a pre-equilibrium step leading to the $\mathrm{Cr(VI)} - \mathrm{S}$ complex [1–3] which experiences the redox decomposition (2e-transfer) at the rate determining step (rds). In the oxidation of alcohols or aldehydes or hydroxy acids, very often the rate determining step involves the breaking of a C–H bond in a cyclic transition state, i.e. chromate ester. This is demonstrated by the positive primary kinetic isotope effect by comparing the reactivity of C–H bond and C–D bond [3,53–58].

Schemes 6 and 7 differ in the fate of the intermediate Cr(IV) and the mode of generation of Cr(V). In strongly acidic media, generally Cr(V) and Cr(IV) remaining as aqua complexes [2,15,59] are more reactive than Cr(VI) and consequently, both the schemes lead to the same rate law. In such cases, the rate of disappearance of Cr(VI) does not depend on the reactivity of Cr(V) and Cr(IV). This is why, it is not possible to discriminate between these two mechanisms kinetically. However, the Rocek mechanism is now widely accepted to explain the Cr(VI) oxidation of varieties of organic substrates [60–76]. Some authors have suggested the simultaneous operation of both the schemes depending on the conditions [2,77]. At higher [Cr(VI)]/[S] ratio, the Westheimer mechanism is favored, while at the low values of the ratio, the Rocek mechanism is favored. In the Rocek mechanism (Scheme 7), the free-radicals are suggested to be responsible for the acrylonitrile polymerization while in the Perez-Benito and co-workers' mechanism [43,44], the carbo-cationic center generated through the hydride transfer towards Cr(IV) is supposed to be responsible for the polymerization of monomer.

Depending on the conditions, Mn(II) can catalyze or inhibit or remain without any effect in the reduction of Cr(VI) [2,15(a),18,43,44,48,49,77–86]. For the one equivalent reduction of Cr(VI) at the rate determining step, many workers have suggested that the rate of Cr(VI) reduction is not affected by Mn(II) [82]. But this conclusion is not always valid [2]. In strongly acidic media, Cr(IV) selectively oxidizes Mn(II) and the rate of Cr(VI) reduction is retarded [43,44,49]. Sometimes, Mn(II) can catalyze the disproportionation of Cr(IV)-complexes (e.g. ehba complex), but it cannot affect the disproportionation of the corresponding Cr(V) complex [15(a),48]. Based on these arguments, Mn(II) was considered as a selective trap to identify the Cr(IV) species, if produced, during the reduction of Cr(VI). But, this conclusion has been disputed by some authors [2,18,85]. In fact, in some cases, Cr(V)–complexes produced as intermediates during the reduction of Cr(VI) can also oxidize Mn(II) [2,85]. Inhibition of the oxidative cleavage of DNA by Mn(II) in the system, Cr(VI)-reductant, is not due to the removal of Cr(IV) intermediate but due to the reduction of oxidized DNA intermediate by Mn(II) [18]. In fact, the fate of Mn(II) in the system, Cr(VI)-reductant, depends on the experimental conditions such as the acidity of the reaction medium, nature of the reductant, etc. Thus, Mn(II) cannot always be considered as the selective trap for Cr(IV).

The generation of the labile intermediates Cr(IV) and Cr(V) during the reduction of Cr(VI) and their implication in explaining the Cr-induced toxicity [2,4–13] have earned the attention of several workers to explore their activity and chemistry [1,2,14–19]. In the oxidation of organic substrates, Cr(V) and Cr(VI) are the major species responsible for C–H bond rupture while Cr(IV) is responsible for C–C bond rupture [50,87]. The ligands like 2-hydroxyacids, diols, sugars, etc. possessing two oxygen atoms capable of forming the five membered rings about the metal center are quite important to stabilize the hypervalent oxidation states of chromium [1,2,14,15(a),42,46-48,61,62,65,66,69,71,73,74]. Amino acids and peptides can also stabilize these states [88,89]. This type of chelation can be attained by the reductants themselves or by the products or by the externally added chelating ligands. Cr(IV) reacts inherently faster than Cr(VI) and the reactivity of Cr(V) largely depends on its stabilization through chelation. If Cr(V) exists in solution in a sufficiently small concentration and reacts faster than Cr(VI) towards a particular substrate, then it does not complicate the kinetic parameters obtained from the absorbance measurement at 350 nm (where both Cr(V) and Cr(VI) strongly absorb in aqueous acid media), but the interpretation becomes complicated when both Cr(VI) and Cr(V) react at comparable rates [66,69,90,91]. The good linear plot of ln(Abs) (at 350 nm) versus time indicates that Cr(V) reacts faster than Cr(VI) [61,71,73]. In many cases, the overall reactivity has been reported [92–94] without any discrimination of the individual contribution of Cr(VI) and Cr(V). When Cr(VI) and Cr(V) react at comparable rates, the consecutive reaction is [66,69,91] (Scheme 8)

The rate constants k_5 and k_6 for the said consecutive reaction can be evaluated from the measurement of absorbance at 350 nm by using the molar absorptivity of Cr(VI) and Cr(V) [66,69,91]. If, $k_5 \gg 2k_6$, Cr(V) does not interfere with the absorbance due to Cr(VI) at 350 nm and k_6 can be

$$\mathrm{Cr(VI)} \xrightarrow[k_6]{\mathrm{S}} \mathrm{Cr(IV)} \xrightarrow[\text{(fast)}]{\mathrm{S+Cr(VI)}} \mathrm{Cr(V) + P + Cr(III)};\ \mathrm{Cr(V)} \xrightarrow[k_5]{\mathrm{S}} \mathrm{P + Cr(III)} \qquad (4.10)$$

Scheme 8.

simply computed from the linear plot of ln(Abs) (at 350 nm) versus time. When Cr(V) reacts faster than Cr(VI), the rate of oxidation by Cr(V) may be measured from peak to peak height of the Cr(V)-EPR signal as a function of time period [61,73].

In the reduction of Cr(VI), in many cases, the kinetics of reduction of Cr(V) species has been followed [61,66,69,73,90,91]. In the reduction of different types of sugars and their derivatives by Cr(VI), the intermediate Cr(V) species, which undergo chelation with the sugar molecules, have been identified by Sala and co-workers [61,62,65,66,69,71,73,74]. Depending on the degree of stabilization of Cr(V), in some cases, Cr(V) reacts faster than Cr(VI) and in some cases both Cr(V) and Cr(VI) react at comparable rates. The reactivity of Cr(VI) and Cr(V) towards the reducing sugars has been explained from their structural features.

The ligands like hmba, ehba, (−)quinate can stabilize both the Cr(IV) and Cr(V) species [2,15(a),46–48]. The reduction of Cr(VI) by strict two-equivalent reductants like As(III) in a buffer solution with the title ligands produce exclusively the bis-chelates with oxochromate(IV) [15(a),46,47]. When the reductants can participate in both the 1e- and 2e-reduction, then, in the presence of suitable ligands, both the Cr(IV) and Cr(V) chelates are produced. Inherently, the Cr(V) chelate is more stable. The Cr(V)–peptide and amino acid (non-sulfur containing) complexes can be prepared from the reaction of Cr(VI) with methanol (that also acts as the solvent) in the presence of the peptide and amino acids [88,89].

Different workers [4,78,86,95–105] have carried out the kinetics of oxidation of different thiol compounds by Cr(VI). It has been suggested that the Cr(VI)-thiol (specially glutathione) interaction in biological systems is quite important to understand the mechanism of Cr-induced toxicity [2,4–13]. A common fact of this interaction is the formation of a distinct orange colored 1:1 chromate-thiol complex (ester-like product) that subsequently undergoes electron transfer reactions. The Cr(VI)–thioester may experience 1e-transfer giving rise to the Cr(V)-intermediate and thiyl radical or react with a second thiol molecule to produce a Cr(IV)-intermediate and disulfide product through 2e-transfer. The 1e-transfer pathway is more important at the lower thiol concentrations (Scheme 9).

$$\mathrm{Cr(VI) + RSH} \rightleftharpoons \mathrm{Cr(VI)–SR + H^+} \qquad (4.11)$$

$$\mathrm{Cr(VI)–SR + RSH} \longrightarrow \mathrm{Cr(IV) + RSSR + H^+} \qquad (4.12)$$

$$\mathrm{Cr(VI)–SR} \longrightarrow \mathrm{Cr(V) + RS^\bullet} \qquad (4.13)$$

Scheme 9.

At pH ≥ 7, the reaction with glutathione is biphasic while for penicillamine it is monophasic [105]. For glutathione, in the first step, the adduct is formed in a reversible step and the second step leads to the redox decomposition of the adduct. In the case of penicillamine, the rate determining step involves the formation of an ester intermediate that undergoes dissociation very rapidly. Compared to glutathione, the coordinated penicillamine is a better electron donor because of the presence of two electron-releasing methyl groups. Different workers have suggested the existence of different intermediates, viz., Cr(V) and Cr(IV) in Cr(VI)-thiol interaction. The sequential one-electron reduction of Cr(VI) to Cr(III) (i.e. Cr(VI) → Cr(V) → Cr(IV) → Cr(III)) by L-cysteine in neutral aqueous solutions has been explained [97] by considering the steps: (i) formation of a Cr(VI)-complex with two cysteine ligands, (ii) its conversion to a Cr(III) complex by the sequential one-electron reductions with the cysteine molecules.

Wiberg and Szeimies [106] have suggested the stepwise 1e-reduction of Cr(VI) to Cr(III) in the reaction with arylamines in acetic acid media. A similar reaction mechanism is known for the reaction with the 1e-reductants of transition metal ions [41] and $[Fe(phen)_3]^{2+}$ [107]. In some other cases, this mechanism has also been suggested [82,97,108–111]. In the oxidation of alkyl/aryl and diphenyl sulfides by Cr(VI), to explain the excellent correlations obtained between the log *k* values and the oxidation potentials/ionization energies of the sulfides and the absence of any rate retardation in the presence of Mn(II), the one-electron transfer mechanism (i.e. Cr(VI) → Cr(V)) at the rate determining step has been proposed [82]. From the effect of Mn(II) on the rate of reduction of Cr(VI), such straight-forward conclusion can never be made [2].

In the interaction of Cr(VI) with ascorbic acid in aqueous acid media, different authors have suggested different mechanisms [17(a),77,85,108-110,112,113] depending on the conditions. The Cr(V)-complex and ascorbate anion radical were confirmed through an EPR study [17(a),77,85,110]. Stearn and Wetterhahn [77] have suggested the rate determining 2e-redox decomposition of the Cr(VI)-ascorbate complex produced in small steady-state concentrations in neutral aqueous solution. Then Cr(IV) may either react with the substrate as a 1e-oxidant (i.e. Rocek mechanism) or react with Cr(VI) to generate Cr(V) (i.e. Westheimer mechanism) depending on the relative values of the ratio [Cr(VI)]/[S] [77]. Other groups of workers [108,109,112] have suggested the formation of the ester-like intermediate at the rate determining step. Dasgupta and co-workers [108,109] have argued that the three successive 1e-transfer steps [i.e Cr(VI) → Cr(V) → Cr(IV) → Cr(III)] occur extremely fast to produce the Cr(III)-product and consequently no appreciable buildup of the Cr(VI)–ester like intermediate occurs.

In explaining the oxidation of organic sulfides in organo-aqueous acid media, two different mechanisms – one involving the nucleophilic attack of sulfide on chromium and the other involving an electron transfer to Cr(VI) leading to Cr(V) at the rate determining step, have been proposed [114,115]. The actual mechanism may be a continuum between these two extreme possibilities – nucleophilic substitution (S_N2) and single electron transfer (SET) [116].

Another interesting mechanism (Scheme 10) has been proposed by Haight et al. [117] and the mechanism is quite similar to the Westheimer mechanism (Scheme 6).

$$Cr(VI) + S \rightleftharpoons Cr(VI)\text{–}S \quad (4.4)$$
$$Cr(VI)\text{–}S \longrightarrow Cr(IV) + P \quad (4.5)$$
$$2Cr(IV) \longrightarrow Cr(V) + Cr(III) \quad (4.14)$$
$$Cr(V) + S \longrightarrow Cr(III) + P \quad (4.7)$$

Scheme 10.

However, a serious limitation to this mechanism is that it requires an accumulation of the Cr(IV) intermediate in high concentrations enough to make its second-order disproportionation possible. This is unfavorable as Cr(IV) reacts very fast with Cr(VI) [1]. In fact, this disproportionation is possible if the substrate is quite unreactive towards Cr(IV). This is why, this Scheme is applicable only in some limited cases [1,81,118,119].

One step 3e-reduction leading to Cr(VI) to Cr(III) has been argued by Rocek and co-workers [120] to explain the cooxidation of two different substrates (e.g. alcohol + oxalic acid) or the oxidation of single substrates like oxalic acid, α-hydroxy acids, etc. In the bis-complex (that is a ternary complex in the case of cooxidation), four functional groups are involved (Scheme 11).

groups are involved.

$$Cr(VI) + 2S \rightleftharpoons Complex \quad (4.15)$$
$$Complex \longrightarrow P + R^{\bullet} + Cr(III), (rds) \quad (4.16)$$
$$Cr(VI) + R^{\bullet} \longrightarrow Cr(V) + P \quad (4.9)$$
$$Cr(V) + S \longrightarrow Cr(III) + P \quad (4.7)$$

Scheme 11.

For the oxidation of a single substrate, this 3e-transfer pathway at the rate determining step is preferred at lower Cr(VI) concentrations in less acidic media while the 2e-transfer pathway (Scheme 7) is preferred at higher Cr(VI) concentrations in strongly acid media. Though this 3e-transfer pathway has been disputed by some workers [1], some authors are still in favor of this mechanism in many cases [79,80,91,121–126]. Recently, we have shown [121] that the micellar effect is an indirect evidence in favor of the 3e-transfer pathway for the cooxidation of oxalic acid and formic acid in aqueous acidic media. In the oxidation of 2-hydroxy-3-methylbutanoic acid by Cr(VI) to 2-methylpropionic acid and CO_2 by C–C cleavage in the presence of excess substrate over [Cr(VI)], the proposed mechanism [124] involves the formation of a 1:1 complex that decomposes by a 3e-transfer step. Cr(V) formed in the subsequent steps, decays faster than Cr(VI) as observed by the EPR study. The given mechanism is outlined in Scheme 12.

$$(CH_3)_2CHCH(OH)CO_2H + HCrO_4^- \rightleftharpoons A^- (complex) \quad (4.17)$$
$$A^- + H_2O \longrightarrow (CH_3)_2CHCO_2H + {}^{\bullet}CO_2^- + Cr(III) \quad (4.18)$$
$$A^- + H^+ \rightleftharpoons AH^+ \longrightarrow (CH_3)_2CHCO_2H + {}^{\bullet}CO_2^- + Cr(III) \quad (4.19)$$
$${}^{\bullet}CO_2^- + Cr(VI) \longrightarrow CO_2 + Cr(V) \quad (4.20)$$
$$Cr(V) + 2(CH_3)_2CHCH(OH)CO_2H \rightleftharpoons B^- (complex) \quad (4.21)$$
$$B^- \longrightarrow (CH_3)_2CHCO_2H + HCO_2H + Cr(III) \quad (4.22)$$

Scheme 12.

The complex B^- has been suggested from the EPR data. The five coordinate oxochromate(V) square pyramidal complex probably binds two molecules of the hydroxy acid acting in a bidentate fashion through the hydroxy and carboxylic acid group. Cr(V) here reacts much faster than Cr(VI).

Thus it is evident that different mechanisms suggest different routes of formation of the intermediate Cr(V): disproportionation of Cr(IV) (cf. Scheme 10), comproportionation of Cr(IV) in the reaction with Cr(VI) (cf. Scheme 6), 1e-reduction of Cr(VI), oxidation of Cr(II) by Cr(VI) (cf. Scheme 5). These different possibilities depend on the nature of the substrates and reaction conditions like [Cr(IV)]/[S] ratio, acid concentration, etc. Stabilization of the labile intermediates Cr(IV) and Cr(V) may govern the mechanistic pathway of reduction of Cr(VI) to Cr(III).

5. Micellar effects on the kinetics of Cr(VI) oxidation of different types of organic substrates

5.1. Oxidation of alcohols

Rodenas and co-workers [127] have investigated the effect of sodium dodecyl sulfate (SDS) micelles on the oxidation of different water soluble alcohols (e.g. 1-butanol, 2-propanol, benzyl alcohol) and water insoluble alcohols (e.g. 1-hexanol, 1-octanol) by chromic acid. The rate increases with the [SDS] for the water soluble alcohols and it attains a limiting value at higher [SDS], while for the water insoluble alcohols, the rate reaches a maximum value and then it decreases with [SDS]. It has been suggested that the acid catalyzed reaction in the micellar phase occurs between the micellized alcohol and chromic acid in the aqueous phase across the boundary. The results of the acid catalyzed oxidation of the alcohols have been explained by considering the pseudo-phase ion-exchange model by assuming the competitive distribution of the micellar counterions and H^+ ions with the micellar head group.

$$H_W^+ + Na_M^+ \rightleftarrows H_M^+ + Na_W^+ \quad (3.22)$$

The influence of sodium dodecyl sulfate (SDS) reverse micelles in 1-butanol, 1-hexanol or 1-octanol on the oxidation of the corresponding alcohol by Cr(VI) in $HClO_4$ medium has been also investigated by Rodenas and Perez-Benito [128]. To explain the kinetic results, it was necessary to consider the intermicellar exchange of the reactants. This exchange depends on the thickness of the layer where the surfactant and alcohol are located. The thickness of the layer was obtained from fluorescence quenching measurement.

Recently, the micellar effects on the Cr(VI) oxidation of different aliphatic alcohols (e.g. ethanol, propanol, butanol) and aromatic alcohols (e.g. benzyl alcohol) in aqueous acid media have been followed by us [129,130]. The micellar effects are different for different types of alcohols and these are quite important from the standpoint of understanding their mechanistic pathways. In the case of alkanols, the cationic surfactant *N*-cetylpyridinium chloride (CPC) has been found to inhibit the process while the anionic surfactant SDS has been found to catalyze the process. Interestingly, for the aromatic alcohol like benzyl alcohol, both the cationic and anionic surfactants catalyze the process. These different types of micellar effects originate from their different types of H^+ dependence. In general, the H^+ -dependence (both in the presence and absence of the surfactants) for the oxidation of the said alcohols is given by

$$-\frac{\mathrm{d}\ln[\mathrm{Cr(VI)}]}{\mathrm{d}t} = k_{\mathrm{obs}} = k_{1\mathrm{H}}[\mathrm{H}^+] + k_{2\mathrm{H}}[\mathrm{H}^+]^2, \quad \text{at fixed } [\text{alcohol}]_{\mathrm{T}} \gg [\mathrm{Cr(VI)}]_{\mathrm{T}} \qquad (5.1.1)$$

For the aliphatic alcohols, the k_{1H} path is absent while for the benzyl alcohol both the k_{1H} and k_{2H} paths contribute. The rate laws and the observed micellar effects can be interpreted by considering the reaction Scheme 13 (for the sake of simplicity, the water molecules present at the vacant coordination sites of Cr(VI) are not shown in **1** and **2**).

$$\mathrm{H{-}CR_2{-}OH + HCrO_4^- + H^+ \rightleftharpoons H{-}CR_2{-}O{-}CrO_2{-}OH\ (\mathbf{1}) + H_2O},\ K_1 \qquad (5.1.2)$$

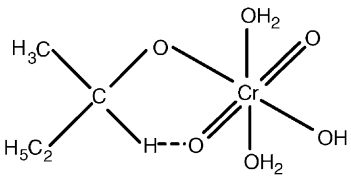
$$\mathbf{1} + \mathrm{H^+} \rightleftharpoons \mathrm{H{-}CR_2{-}O{-}CrO_2{-}OH_2^+}\ (\mathbf{2}),\ K_2 \qquad (5.1.3)$$

$$\mathbf{1} \longrightarrow \mathrm{R_2CO + H_2CrO_3},\ k_1 \qquad (5.1.4)$$

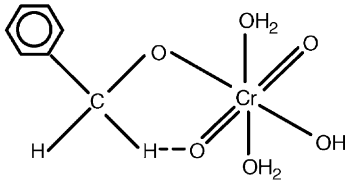
$$\mathbf{2} \longrightarrow \mathrm{R_2CO + H_2CrO_3 + H^+},\ k_2 \qquad (5.1.5)$$

Scheme 13.

If the unprotonated Cr(VI)–ester (**1**) is kinetically active towards the redox decomposition (i.e. reaction 5.1.4) through a hydride transfer pathway, then the k_{1H} path contributes. On the other hand, the protonated species (**2**) explains the k_{2H} path (i.e. reaction (5.1.5)). The hydride transfer mechanism generates an electron deficient carbon centre that can be stabilized by the phenyl ring (for benzyl alcohol) through resonance and it makes the species (**1b**) kinetically active. For the alkanols, no such stabilizing effect is present and consequently the unprotonated ester (**1a** for alkanol, say 2-butanol) is kinetically inactive. Protonation of the Cr–OH (**2** in Scheme 13 (for the sake of simplicity, the water molecules present at the vacant coordination sites of Cr(VI) are not shown in **1** and **2**)) bond facilitates the electron flow towards Cr(VI) and it is the only pathway for the aliphatic alcohol.



(**1a**)



(**1b**)

It has been proposed that the electrically neutral Cr(VI)–alcohol ester (**1**) is partitioned between the micellar and aqueous phase.

$$\mathbf{1}_{\mathrm{W}} + \mathrm{D}_n \rightleftarrows \mathbf{1}_{\mathrm{M}} \qquad (5.1.6)$$

The species **1** is preferentially accumulated on the micellar surface (Stern layer) with the hydrophobic groups (i.e. alkyl or aryl groups) projecting towards the hydrophobic core. In other words, the reactants H_2CrO_4 (that is kinetically active) [114,127,128] and ROH are partitioned in the micellar (both cationic and anionic) pseudo-phase as follows:

$$[\mathrm{H_2CrO_4}]_{\mathrm{W}} + \mathrm{D}_n \rightleftarrows [\mathrm{H_2CrO_4}]_{\mathrm{M}} \qquad (5.1.7)$$

$$[\mathrm{ROH}]_{\mathrm{W}} + \mathrm{D}_n \rightleftarrows [\mathrm{ROH}]_{\mathrm{M}} \qquad (5.1.8)$$

Thus the aqueous phase is depleted while the micellar phase is enriched with the reactants.

Here it is important to discuss the nature of Cr(VI) species that remains bound on the micellar surface (i.e. Stern layer). In aqueous acidic systems (without any surfactant), the predominant species is $HCrO_4^-$ that remains in an equilibrium with $Cr_2O_7^{2-}$. Under the present experimental conditions, concentrations of the higher oligomers are negligibly small. The protonation equilibrium, $HCrO_4^- + H^+ \leftrightarrows H_2CrO_4$, is highly favored to the left side (protonation constant ≈ 0.2 [111]). In the micellar media, to facilitate the binding of Cr(VI) species on the micellar surface, formation of H_2CrO_4 is favored through the protonation of $HCrO_4^-$ [114,127,128]. Binding of the anionic species, $HCrO_4^-$ on the anionic micellar surface (e.g. SDS) is unfavorable due to an electrostatic repulsion, but the neutral species H_2CrO_4 can bind on the micellar surface through an ion–dipole interaction and hydrogen bonding [114,127–130]. This binding constant has been estimated in many cases [114]. Thus

the binding of Cr(VI) species on the anionic micellar surface of SDS in an acidic condition supports the existence of H_2CrO_4 on the micellar surface. In fact, Cr(VI) as H_2CrO_4 can bind with the micellar surface of both the cationic and anionic surfactants [114,127–130].

The ester (**1b**) of benzyl alcohol is kinetically active and consequently, the reaction in both the micellar phases (i.e. cationic and anionic) goes on through the k_{1H} path. For benzyl alcohol, the interaction between the π-electron cloud of the phenyl group and the cationic head group of CPC favors its partitioning. For the k_{2H} path, protonation of the ester (**1**) is required and the approach of proton towards the cationic micellar pseudo-phase is repelled. Thus CPC disfavors the k_{2H} path in the micellar pseudo-phase and consequently the reaction is restricted to go on only in the aqueous phase that is depleted in reactant concentration. The anionic micellar head groups favor the partitioning of the H^+ ion in the micellar phase to favor the k_{2H} path. Thus, SDS favors both the k_{1H} and k_{2H} paths and CPC favors the k_{1H} path (that is absent for the alkanols) but disfavors the k_{2H} path. The rate data were subjected to analysis by the Piszkiewicz model [36] and the binding constants have been evaluated. From the small values of n (cooperative index), it has been concluded that the submicellar aggregates are kinetically active.

Recently, the micellar effects on the Cr(VI) oxidation of diols [131], D-mannitol [132], D-sorbitol [132] and formaldehyde [133] in the presence and absence of picolinic acid (PA) in aqueous acid media have been studied. The rate laws are the same in presence and absence of the surfactants. In such cases, the PA-catalyzed path goes on along with the slower uncatalyzed path.

$$-\frac{\mathrm{d}\ln[\mathrm{Cr(VI)}]}{\mathrm{d}t} = k_{\mathrm{obs(T)}} = k_{\mathrm{obs(u)}} + k_{\mathrm{obs(c)}} = k_{\mathrm{obs(u)}} + k_{\mathrm{cat}}[\mathrm{PA}]_{\mathrm{T}} \quad (5.1.9)$$

It has been noticed that both the uncatalyzed (i.e. $k_{\mathrm{obs(u)}}$) and PA-catalyzed (i.e. $k_{\mathrm{obs(c)}}$) paths are inhibited by CPC while these paths are catalyzed by SDS. Kinetically, the diols and polyols behave like the monohydric alcohols and the uncatalyzed path can be explained by considering the reaction Scheme 13 (for the sake of simplicity, the water molecules present at the vacant coordination sites of Cr(VI) are not shown in **1** and **2**). The kinetically active form of formaldehyde is $H_2C(OH)_2$ [133] and it also experiences the esterification step like the alcohols. For all these substrates, the uncatalyzed path shows the second-order dependence on $[H^+]$ while the PA-catalyzed path shows a zeroth order dependence on $[H^+]$, i.e

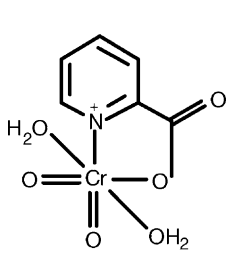
$$k_{\mathrm{obs(u)}} = k_{\mathrm{H(u)}}[\mathrm{H}^+]^2 \quad (5.1.10)$$

$$k_{\mathrm{obs(c)}} = k_{\mathrm{H(c)}}[\mathrm{H}^+]^0 \quad (5.1.11)$$

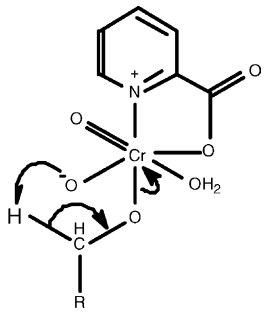
The micellar effect on the uncatalyzed path has been explained in the same way as in the case of aliphatic alcohols. For the PA-catalyzed path, the proposed reaction mechanism has considered the following reactions leading to the formation of the kinetically active cyclic Cr(VI)–PA complex (**5**) in a rapid pre-equilibrium step (Eq. (5.1.12)).

$$\mathrm{PA} + 2\mathrm{H}^+ + \mathrm{HCrO_4}^- \rightleftarrows \mathbf{5} + 2\mathrm{H_2O} \quad (5.1.12)$$

$$\mathbf{5} + \mathrm{RCH_2OH} \rightleftarrows \mathbf{6} + \mathrm{H}^+ \quad (5.1.13)$$



(**5**)



(**6**)

The active oxidant (**5**) interacts with the substrate (denoted by R_2CHOH having at least one alcoholic OH group) to produce the ternary complex (**6**) that experiences the redox decomposition. The active oxidant (**5**) being cationic is preferably accumulated in the anionic micellar surface of SDS but it is repelled by the cationic micellar head groups.

$$\mathrm{Ox_W}^+ + \mathrm{Na_M}^+ \rightleftarrows \mathrm{Ox_W}^+ + \mathrm{Na_W}^+ \quad (5.1.14)$$

For the both types of surfactants, the Stern layer is enriched with the organic substrate projecting the alkyl group towards the hydrophobic core. Thus, for SDS, the micellar pseudo-phase accumulates both the reactants while CPC accumulates the substrate only keeping the oxidant (**5**) exclusively in the aqueous phase. For SDS, the reaction goes on in both the aqueous phase and micellar phase that preferentially accumulates both the reactants. It explains the rate enhancement. CPC restricts the reaction only in the aqueous phase that is depleted in the substrate concentration. It explains the micellar inhibition.

In the Cr(VI) oxidation of cyclopentanol [134] in the presence of sodium dodecyl sulfate (SDS), it has been noticed that after the cmc, the rate decreases monotonically with increasing [SDS]. This observation has been explained by using the Menger–Portnoy model [34] that considers the solubilization of one reactant only into the micellar phase. The modified Menger–Portnoy equation [35], which neglects the k_M-path (reaction in the micellar phase), is

$$\frac{1}{k_\psi} = \frac{1}{k_W} + \frac{KC}{k_W} \quad (5.1.15)$$

Here K gives the binding constant of the species that is partitioned between the aqueous phase and micellar phase. This species has been argued to be the oxidant. The binding constant determined by using the Berezin's equation (in which k_M is neglected and binding of one reactant only with the micellar phase is considered) nicely agreed with that

obtained from Eq. (5.1.15). It has been noted that k_Ψ decreases exponentially with increasing [K_2SO_4]. It has been explained by considering the change of surface potential with the addition of salt K_2SO_4.

SDS has been found to catalyze the oxidation of cyclohexanol [135] by Cr(VI) in aqueous acidic media. It has been suggested that the rate enhancement occurs due to the solubilization of both the substrate and oxidant in the micellar phase. The reaction predominantly occurs in the micellar pseudo-phase. The catalysis can be rationalized by an increase in the stabilization of the positively charged Cr(VI)–cyclohexanol complex (protonated) in the negatively charged micellar pseudo-phase due to the electrostatic attraction. To explain the kinetic data, the phase separation model of Berezin et al. [30], applicable to the cases in which both the reactants, i.e. chromic acid and cyclohexanol, are strongly bound to the micellar phase was applied. The binding constants and rate constant were estimated graphically. The high binding constants and partition coefficients were attributed, respectively to the hydrophobic and electrostatic binding of the substrate and the oxidant, respectively to the micelle. To understand the striking difference of micellar effect on the Cr(VI) oxidation of the closely related substrates cyclopentanol and cyclohexanol, it needs more work.

Some authors [23(a),134,135] have considered the formation of $H_3CrO_4^+$ species (through the protonation of H_2CrO_4) as the active Cr(VI) species that is attracted to the micellar head groups of SDS. But formation of $H_3CrO_4^+$ is quite unlikely under their experimental conditions. The protonation constant of H_2CrO_4 is of the order of 10^{-6} [111]. In fact, in a fairly strong acid solution (even up to 3.6 mol dm^{-3} $HClO_4$ solution), no further protonation of H_2CrO_4 occurs and Cr(VI) is distributed as $[Cr(VI)]_T = [H_2CrO_4] + [HCrO_4^-]$ [136]. The preferential partitioning of H_2CrO_4 in the Stern layer may be explained by considering the ion–dipole interaction and hydrogen bonding interaction with the micellar head groups and in fact, the binding of H_2CrO_4 on SDS has been reported in many cases [114,129,130]. The reactions are acid catalyzed and the H^+ ions are preferably partitioned in the anionic micellar pseudo-phase. Thus the favored partitioning of both H_2CrO_4 and H^+ ions in the micellar pseudo-phase can explain the origin of micellar catalysis [23(a),134,135] without considering the formation of the species $H_3CrO_4^+$.

5.2. Oxidation of sugars

The micellar effect on both the picolinic acid (PA) catalyzed and uncatalyzed paths of Cr(VI) oxidation of different reducing sugars (both aldohexoses and ketohexoses denoted by S–OH) in aqueous acid media has been studied by us [137–139]. The rate laws in absence of the surfactants remain unchanged in the presence of the surfactants. Kinetically, the reducing sugars are just like the polyols in which the reactivity of the alcoholic OH groups is expected to be influenced by the carbonyl group. Though hydroxyacetone is more reactive than glycol, but no such enhanced reactivity of the sugars is noticed [131,137–139]. It occurs so because of the very small concentration of the open-chain form of the sugars that predominantly exist in the cyclic forms. SDS catalyzes both the uncatalyzed and PA-catalyzed paths while CPC inhibits both the pathways. In the case of ketose, the glycol splitting leads to lactone of C_5-aldonic acid while for the aldohexose no glycol splitting occurs and the product is aldonic acid. The uncatalyzed path goes through the ester formation of chromic acid and it needs protonation for the redox decomposition. The observed micellar effect on the uncatalyzed path (that shows a second-order dependence on [H^+]) has been explained (Scheme 14 (for the sake of simplicity, water molecules present at the vacant coordination sites of Cr(VI) are not shown in Eqs. (5.2.1) and (5.2.3))) as in the case of alcohols.

For the PA-catalyzed path, the Cr(VI)–PA positively charged complex (**5**) forms a ternary complex with the sugar and then the ternary complex experiences the redox decomposition. The inhibition by CPC indicates that the active oxidant remains mainly in the aqueous phase (cf. Eq. (5.1.14)) where the substrate concentration is depleted. The catalysis by SDS indicates that the reaction goes on in both the aqueous and micellar phase in which the reactants are preferably concentrated. The plot of k_{obs} versus [SDS] (for both the uncatalyzed and PA-catalyzed paths), it is found that the rate initially increases, but it tends to level off at higher [SDS]. In fact, an increase in [SDS] increases the concentration of micellar counterions (i.e. Na^+) that may displace H^+ and Ox^+ ions out of the micellar surface to drive the equilibria (3.22) and (5.1.14) to the left hand directions. It reduces [$H_M{}^+$] and [$Ox_M{}^+$] to inhibit the rate process in the micellar phase. Due to these opposing factors (i.e. dilution of all reactants over the micelles at higher [SDS]), k_{obs} initially increases with [SDS], but it attains a limiting value at higher [SDS]. To explain the observed micellar effect and to estimate the binding constants, the rate data were subjected to analysis by the Menger–Portnoy model [34] and cooperative model [36].

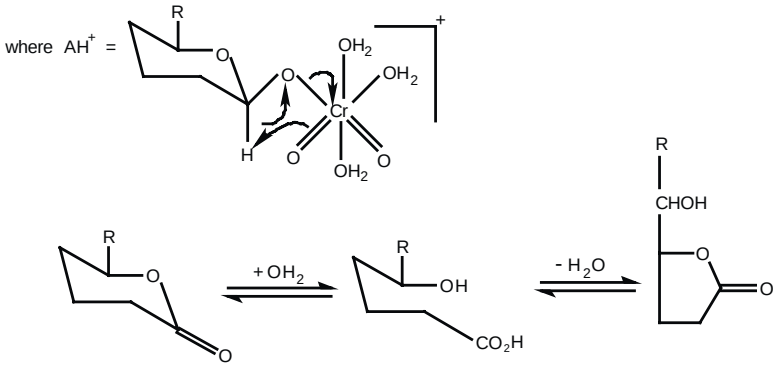
The micellar effects on the chromic acid oxidation of D(+)-xylose have been studied by Kabir-ud-Din and co-workers [23(a)]. The rate law and the mechanism for the reaction are the same in the absence and presence of the surfactants like SDS and Triton X-100 (*tert*-octylphenoxypolyethoxyethanol). The observed rate constant has been found to increase monotonically with the increase of surfactant concentration. The observed micellar catalysis has been interpreted by considering the simultaneous partitioning of both the reactants (i.e. H_2CrO_4 and xylose) between the aqueous and micellar pseudo-phase (that is the Stern layer). The binding force orginates from the ion–dipole interaction (in SDS) and hydrogen bonding interaction (in Triton X-100 using the ether oxygen of polyoxyethylene). As the reaction is acid catalyzed, the required H^+ ions are also partitioned in the micellar phase through an electrostatic attraction in SDS and through an ion–dipole

$$S\text{–}OH + HCrO_4^- + H^+ \rightleftharpoons S\text{–}OCrO_3H\ (\mathbf{A}) + H_2O,\ K_1 \quad (5.2.1)$$

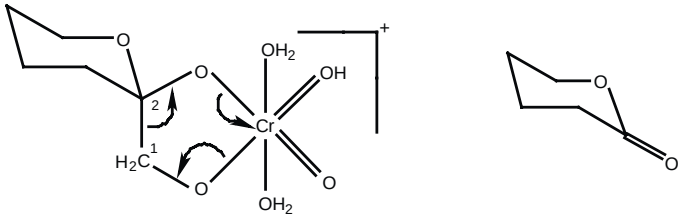
$$\mathbf{A}_W + D_n \rightleftharpoons \mathbf{A}_M \quad (5.2.2)$$

$$\mathbf{A} + H^+ \rightleftharpoons S\text{–}OCrO_3H_2^+\ (\mathbf{AH}^+),\ K_2 \quad (5.2.3)$$

$$\mathbf{AH}^+ \longrightarrow \text{product}\ (\mathbf{P}) + Cr(IV),\ k_1 \quad (5.2.4)$$



(For aldohexose like D-glucose with R = —CH_2OH)



(AH^+) **(P)**

(For ketohexose like D-fructose)

Scheme 14.

interaction in Triton X-100. The observed micellar catalysis in the case of SDS has been found to be retarded by the ions like NH_4^+, Li^+ and Na^+. It is suggested that the addition of such ions from the external electrolyte will exclude the required H^+ ions from the micellar phase through the ion-exchange process. Consequently, the H^+-catalyzed reactions will be retarded. The similar cases of inhibition of micellar catalysis by the added salts have been noted in many cases [35,140,141].

5.3. Oxidation of different types of carboxylic acids

The kinetic studies of oxidation of lactic acid [142] and DL-mandelic acid [143] by Cr(VI) in aqueous acidic media in the presence of the anionic surfactant, sodium dodecyl sulfate (SDS) have been studied by Panigrahi and co-workers. The oxidation rate has been found to increase with the surfactant concentration up to the critical micellar concentration (cmc) of the surfactant then it decreases as the surfactant concentration increases further. The Menger–Portnoy model [34], which takes care of solubilization of one reactant only into the micellar phase, has been found inadequate to explain the findings. Considering the partitioning of both the reactants (e.g. organic substrates and H_2CrO_4, suggested to be kinetically active) between the bulk aqueous phase and the micellar pseudo-phase, the kinetic data have been rationalized by the Berezin et al.'s model [30]. The proposed reaction (scheme 15) is given below:

$$S_W + Cr(VI)_W \xrightarrow{k_W} \text{product} \quad (5.3.1)$$

$$K_S \uparrow\downarrow \quad K_{ox} \uparrow\downarrow$$

$$S_M + Cr(VI)_M \xrightarrow{k_M} \text{product} \quad (5.3.2)$$

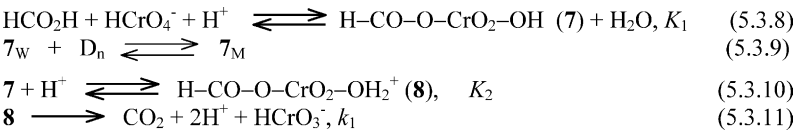
Scheme 15.

In Scheme 15, the organic substrate, i.e. lactic acid or DL-mandelic acid, is denoted by S and the active oxidant species H_2CrO_4 is represented by Cr(VI). According to the Berezin's approach [30], under the conditions P_S, $P_{Ox} \gg 1$, the rate equation is given by

$$k_\Psi = \frac{k_W + k'_M K_S K_{ox} C}{\{(1 + K_S C)(1 + K_{ox} C)\}}, \quad \text{where } k'_M = \frac{k_M}{V} \quad (5.3.3)$$

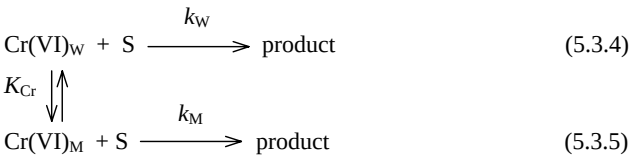
Here the symbols bear the usual significance (cf. Eq. (3.4)). By using Eq. (5.3.3) the different rate constants and binding constants have been evaluated. The decrease of rate at the higher concentrations of surfactant has been subjected to the applicability of the Piszkiewicz model [36] that considers the formation of kinetically inactive reactant–micelle aggregate.

The oxidation of malic acid [144] by Cr(VI) in the presence of SDS is inhibited by the surfactant. The inhibition has been traced to partition the Cr(VI) species as well as the acid concentration, between the aqueous and micellar phase. The results indicate that the reaction occurs in the aqueous phase in the presence of much reduced concentration of H^+ ion. Considering the binding of one reactant (i.e. H_2CrO_4) to the Stern layer of the micelle, the appropriate



Scheme 17.

Berezin et al.'s model [30] (Scheme 16) has been employed to the kinetic data. The proposed reaction paths are shown in Scheme 16.



Scheme 16.

Here Cr(VI) is H_2CrO_4 and S is the organic substrate present at the interface (i.e. Stern layer). The relevant rate law is given by

$$k_\Psi = \frac{k_W + k_M K_{Cr} C}{1 + K_{Cr} C} \quad (5.3.6)$$

The linearity of the plot of $1/k_\Psi$ versus C indicates that $k_W \gg k_M K_{Cr} C$. A similar conclusion has been drawn by using the Menger–Portnoy model [34]. It has been found that the binding constant of the Cr(VI) species increases with the increase of H^+ ion concentration. A similar observation has been noted in the Cr(VI) oxidation of malonic acid [145] in the presence of SDS.

CPC has been found to retard the PA-catalyzed Cr(VI) oxidation of maleic acid [146,147], malic acid [146,147] and formic acid [121,123,148]. The effect of CPC and SDS on the PA-catalyzed paths of Cr(VI) oxidation of these substrates supports the proposed reaction mechanism in which the positively charged complex (**5**) has been identified as the active oxidant.

It is quite interesting to note that CPC inhibits the Cr(VI) oxidation of formic acid [121,123,148] in a monotonic fashion in aqueous sulfuric acid media while under the comparable conditions, CPC catalyzes the oxidation of oxalic acid and then inhibits the reaction after attaining a maximum value in the rate versus $[CPC]_T$ profile [121]. This difference in the observed micellar effect has been explained in terms of their different mechanistic pathways. The observed rate equation (both in the presence and absence of the surfactant) is

$$-\mathrm{d}\ln[\mathrm{Cr(VI)}]/\mathrm{d}t = k_{obs} = k[S]_T^x[H^+]^y \quad (5.3.7)$$

where $x = 2$, $y = 0$ for S = oxalic acid; and $x = 1$, $y = 2$ for S = formic acid. All these observations have been explained by considering the reactions in Scheme 17 (for the sake of simplicity, water molecules present at the vacant coordination sites are not shown in **7** and **8**) for formic acid and Scheme 18 (for the sake of simplicity, water molecules present at the vacant coordination sites are not shown in **9**) for oxalic acid.

The continuous rate retardation by CPC in the case of formic acid is due to the preferential partitioning of the Cr(VI)–substrate ester (**7**) in the micellar pseudo-phase (most probably in the Stern layer). For the redox decomposition of the ester, the proton is not available in the cationic micellar phase. Thus the reaction goes on only in the aqueous phase that is depleted in the active reactant concentration. For oxalic acid, the neutral ester (**9**) is also preferably accumulated on the micellar surface (Stern layer) and then it combines with the oxalate (that is also preferably accumulated on the micellar surface due to an electrostatic attraction) to form a bis-complex (**10**) that experiences the redox decomposition through three electron transfer. It explains the origin of micellar catalysis and supports the mechanism proposed by Rocek and co-workers [120]. At the relatively higher concentrations of the CPC, it is believed that there is a sufficient surfactant concentration to take up all the reactive species through the micellar solubilization and the addition of excess surfactants merely exerts a dilution effect on the solubilized reactant species resulting a gradual decrease of the rate. In other words, the increased concentration of the counterion (i.e. Cl^-) inhibits the reactant species oxalate anion to be accumulated in the micellar phase. The Piszkiewicz model [36] at the higher concentrations of the surfactant considers the formation of the kinetically inactive reactant-surfactant aggregate to explain the micellar inhibition. This model has been examined in the present case in terms of the following relationship.

$$\log Q = \log\left[\frac{k_M}{k_2} - 1\right] = \log K_P + p\log[D],$$

cf. Eq. (3.19)

The different characteristic parameters have been estimated. At the lower surfactant concentrations, the micellar catalysis has been explained in terms of the following relationship (cf. Eq. (3.17)) as suggested in the Piszkiewicz model [36].

The estimated parameters like n (cooperative index, indicating the formation of submicellar active aggregates),

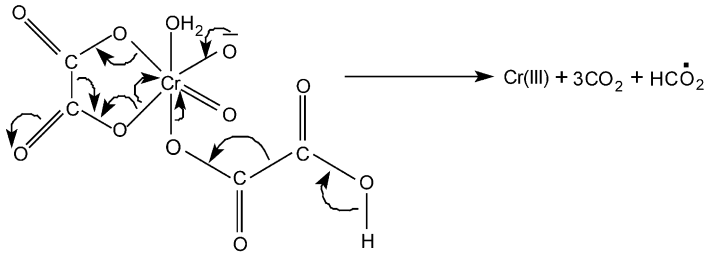
$$H_2C_2O_4 \rightleftharpoons HC_2O_4^- + H^+ \quad (5.3.12)$$

$$H_2C_2O_4 + HCrO_4^- + H^+ \rightleftharpoons CrO_2(C_2O_4)\ (\mathbf{9}) + 2H_2O,\ K_1 \quad (5.3.13)$$

$$\mathbf{9}_W + D_n \rightleftharpoons \mathbf{9}_M \quad (5.3.14)$$

$$[HC_2O_4^-]_W + D_n \rightleftharpoons [HC_2O_4^-]_M \quad (5.3.15)$$

$$\mathbf{9} + HC_2O_4^- \rightleftharpoons (HO_2CCO_2)Cr(O)(O^-)(C_2O_4)\ (\mathbf{10}) \quad (5.3.16)$$



(10)

Scheme 18.

$[CPC]_{50}$ and K_D are in good conformity with the observations.

$$\log G = \log\left[\frac{k_{obs} - k_W}{k_M - k_{obs}}\right] = n\log[D] - \log K_D,$$

cf. Eq. (3.17)

The kinetics and mechanism of Cr(VI) oxidation of glycolic acid in the absence and presence of the cationic surfactants cetyltrimethylammonium bromide (CTAB) and cetyl pyridinium bromide (CPB) are the same [149]. The process is catalyzed by both Mn(II) and the said cationic surfactants. The micellar catalysis has been explained by considering a model in which the reaction rate depends on the concentrations of both the reactants in the micellar pseudo-phase. The rate retarding effect of the inorganic salts like NaCl, NaBr, $NaNO_3$, Na_2SO_4 on the observed micellar catalysis has been explained by considering the removal of glycolic acid from the reaction site. The micellar effect on the kinetics of Mn(II)-catalyzed oxidation of citric acid by Cr(VI) has been studied by the same group in different conditions [79]. The rate determining step involves the one-step three electron transfer in the complex $HCrO_4^-$–citric acid–Mn(II) that is formed in pre-equilibrium steps. In this case, the cationic surfactants like CTAB and CPB show the rate retarding effect while the rate remains unchanged in the presence of the anionic surfactant SDS. The observed micellar effect has been interpreted by considering the reaction occurring in the aqueous phase. The activation parameters are also significantly affected by the said cationic surfactants.

5.4. Oxidation of organic sulfides and sulfoxides

The rate of Cr(VI) oxidation of dimethylsulfoxide (DMSO) is very slow but the corresponding PA-promoted process is fairly fast [150,151]. It is suggested that the Cr(VI)–PA complex formed at the pre-equilibrium step experiences a nucleophilic attack by the S of DMSO to produce a positively charged reactive intermediate (**11**) that experiences an oxygen transfer or a ligand coupling [152] to give the product dimethylsulfone. The reactive intermediate (**11**) may have different possible structures to explain the experimental findings. Some possible structures of the intermediate are shown in **11a,b,c** to explain the oxygen transfer process. The observed micellar effect (i.e. catalysis by SDS and retardation by CPC) is in good conformity with the proposed reaction mechanism. In the presence of SDS, the positively charged oxidant (**5**) experiences a preferential partitioning in the micellar pseudo-phase due to an electrostatic attraction. DMSO (neutral, favorable hydrophobic interaction) is also partitioned in the micellar phase (Scheme 19).

$$(Me_2SO)_W + \mathbf{5}_W \xrightarrow{k_W} \text{product}, \quad (5.4.1)$$

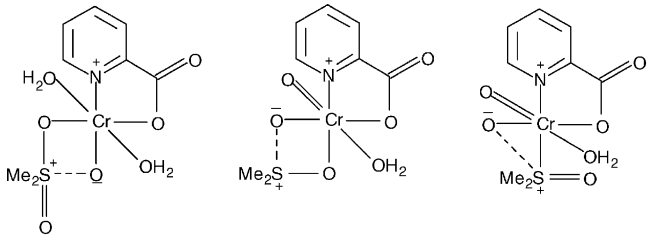
$$K_S \uparrow\downarrow \qquad K_{ox} \uparrow\downarrow$$

$$(Me_2SO)_M + \mathbf{5}_M \xrightarrow{k_M} \text{product}, \quad (5.4.2)$$

Scheme 19.

The overall process is acid catalyzed and this explains why the increase in $[H^+]$ increases $[H_M^+]$ (=concentration of H^+ in the anionic micellar phase, cf. Eq. (3.23)) to accelerate the redox reaction in the micellar phase. This distribution pattern of the reactants can explain the SDS catalysis. In the presence of CPC, the active oxidant remains confined in the aqueous phase due to an electrostatic repulsion by the positively charged cationic micellar head groups. Thus the reaction is mainly restricted in the aqueous phase that is depleted in the concentration of DMSO. The process is acid catalyzed and the approach of H^+ ion towards the micellar phase is also prevented.

At the event of formation of the ternary complex (**11**), there is a buildup of positive charge on the S of DMSO. It is favored in the presence of anionic micellar head groups but disfavored in the presence of cationic micellar head groups.



(11a) **(11b)** **(11c)**

SDS has been found to catalyze the Cr(VI) oxidation of dialkyl sulfides [114] while the cationic surfactant, cetyltrimethylammonium chloride (CTAC) retards the reaction. It has been explained by considering the fact that the reaction takes place both in the aqueous and micellar phase. The reaction is catalyzed by SDS because of the enhanced local concentrations of the reactants in the micellar phase. The reaction is acid catalyzed and the H^+ ion gets preferentially concentrated in the anionic micellar phase. The cationic surfactant inhibits the reaction because the approach of H^+ ion to the cationic micellar surface (in which both the reactants are preferentially concentrated) is unfavorable due to an electrostatic repulsion. Moreover, the oxidation of an organic sulfide involves the electron transfer from sulfide to Cr(VI) and the buildup of positive charge on the sulfur is unfavorable due to a repulsive interaction with the cationic micellar head groups. In fact, this is also in agreement with the observed micellar catalysis in the presence of anionic surfactant, SDS. Here, the change of polarity of the medium (specifically in the intermicellar zone in which the reactants are positioned) with the addition of surfactant to influence the observed micellar effect has been analyzed.

5.5. Oxidation of other types of organic compounds

The effect of surfactants on the oxalic acid catalyzed oxidation of different aromatic azo compounds by Cr(VI) has been investigated by Reddi and co-workers [153]. Both SDS and CTAB (cetyltrimethylammonium bromide) have been found to inhibit the reaction while the non-ionic surfactant, polyoxyethylene(23)dodecanol (Brij 35) catalyzes the reaction. The neutral Cr(VI)–oxalic acid complex has been suggested as the active oxidant. It is preferably accumulated in the aqueous phase in the presence of both the cationic and anionic surfactants but it gets partitioned between the aqueous and micellar pseudo-phase in the presence of the non-ionic surfactant. The aromatic azo-compound is preferably accumulated in the micellar phase due to the hydrophobic interaction in all cases (i.e. SDS, CTAB and Brij 35). These different patterns of partitioning of the reactants in the presence of different types of surfactants can explain the observed micellar effects. The binding parameters have been calculated by analyzing the kinetic data using the Piszkiewicz model [36]. In analyzing the kinetic data, k_M was taken as the maximum value of the observed rate constant for the catalyzed reaction and the lowest value of the observed rate constant for the inhibited reactions. Values of n, $\log[D]_{50}$ (i.e. required concentration of detergent for the half-maximal catalysis or inhibition of the reaction) were estimated graphically. The results indicated the reactant induced micellization and these submicellar aggregates were kinetically important.

The kinetics and mechanism of chromic acid oxidation of ethylenediaminetetraacetic acid (EDTA) in the presence of the non-ionic surfactant Triton X-100 have been studied [154]. The pseudo-first-order rate constant of the process has been found to increase monotonically with the increase of surfactant concentration. The observed micellar catalysis has been rationalized by considering the fact that the reactants bind with the non-ionic micellar head groups (ether oxygen of the polyoxyethylene) through the hydrogen bonding and the reactants are concentrated in the Stern layer. The observed micellar effect has been analyzed by using the cooperative model [36].

6. Application of chromate oxidimetry in presence of surfactants

By selecting a suitable Cr(VI)–substrate indicator reaction, the very low concentrations of the different types of rate accelerating agents can be estimated by using the principle of catalytic kinetic methods of analysis [122]. Synthesis of ketones from the strained and cleavage prone alcohols can be attained through the cooxidation of oxalic acid [50,120]. Besides these applications, the use of surfactants having an amphiphilic character may be immensely helpful in oxidizing the several hydrophobic organic substances by the hydrophilic chromic acid. Generally, it is very difficult to oxidize the hydrophobic substances by the hydrophilic chromic acid because of the hydrophobic-hydrophilic repulsion. In the presence of the aggregates of the amphiphilic surfactant molecules, the hydrophobic substances (dissolved in the micellar core) and the hydrophilic oxidant (bound on the micellar surface) can come close together to facilitate the redox process. Thus the surfactants may catalyze the two phase oxidation [155] of different hydrophobic organic compounds by chromic acid. Sometimes, due to the binding of the oxidant on the micellar surface, the reduction potential of the oxidant may increase to allow the oxidation of comparatively non-reactive substrates [155]. In fact, in some cases, the use of micellar solutions can produce the better yield than the reactions occurring in organic solvents or aqueous solutions. It may give a huge scope for chromate oxidimetry. Moreover, the studies in this direction can provide a better understanding about the chromate toxicity and the electron transfer reactions, in general, occurring at the interface.

7. Conclusions

The review has attempted to explain how the surfactants can modify the redox activity of Cr(VI) in the oxidation of different types of organic substances. The micellar effect can be correlated with the nature of the reducing substrates and the reaction conditions. These micellar effects are quite important to understand and to substantiate the proposed mechanistic pathways. The use of suitable surfactants may facilitate the two phase oxidation of different organic substrates by chromic acid. This may widen the applicability of chromate oxidimetry in organic synthesis.

Acknowledgements

Financial support from CSIR (New Delhi) and Visva Bharati University is thankfully acknowledged.

References

[1] M. Mitewa, P.R. Bontchev, Coord. Chem. Rev. 61 (1985) 241.
[2] R. Codd, C.T. Dillon, A. Levina, P.A. Lay, Coord. Chem. Rev. 216–217 (2001) 537.
[3] M.K. Mahanti, K.K. Banerji, J. Indian Chem. Soc. 79 (2002) 31.
[4] P. O'Brien, G. Wang, J. Chem. Soc., Chem. Commun. 690 (1992).
[5] S.A. Katz, H. Salem, in: The Biological and Environmental Chemistry of Chromium, VCH Publishers Inc., New York, 1994, p. 65.
[6] P. O'Brien, A Kortenkamp, Transition Met. Chem. 20 (1995) 636.
[7] (a) C.B. Klein, in: L.W. Chang (Ed.), Toxicology of Metals, CRC-Lewis Publishers, New York, 1996, p. 205;
(b) A.K. Das, in: Inorganic Chemistry: Biological and Environmental Aspects, Books and Allied, Kolkata, in press.
[8] X. Shi, A. Chiu, C.T. Chen, B. Halliwell, V. Castranova, V. Vallyathan, J. Toxicol. Environ. Health. Part B 2 (1997) 87.
[9] M. Costa, Crit. Rev. Toxicol. 27 (1997) 431.
[10] S. De Flora, Carcinogenesis 21 (2000) 533.
[11] M. Cieslak-Golonka, Polyhedron 15 (1996) 3667.
[12] (a) D.M. Stearns, K.E. Wetterhahn, NATO ASI Series, Series 2, 1997, p. 55;
(b) D.M. Searns, K.E. Wetterhahn, Chem. Res. Toxicol. 10 (1997) 271;
(c) K.D. Sugden, K.E. Wetterhahn, Inorg. Chem. 35 (1996) 651;
(d) K.D. Sugden, K.E. Wetterhahn, Inorg. Chem. 35 (1996) 3727;
(e) K.D. Sugden, K.E. Wetterhahn, Chem. Res. Toxicol. 10 (1997) 1397;
(f) K.D. Sugden, J. Inorg. Biochem. 77 (1999) 177.
[13] (a) A. Kortenkamp, M. Casadevall, P. da Cruz Fresco, R.O.J. Shayer, NATO ASI Series, Series 2, 1997, p. 15;
(b) A. Levina, G. Barr-David, R. Codd, P.A. Lay, N.E. Dixon, A. Hammershoi, P. Hendry, Chem. Res. Toxicol. 12 (1999) 371.
[14] (a) E.S. Gould, Acc. Chem. Res. 19 (1986) 66;
(b) D.K. Geiger, Coord. Chem. Rev. 164 (1997) 261.
[15] (a) E.S. Gould, Coord. Chem. Rev. 135–136 (1994) 651;
(b) A. Bakac, J.H. Espenson, Acc. Chem. Res. 26 (1993) 519;
(c) M.C. Ghosh, E.S. Gould, J. Am. Chem. Soc. 115 (1993) 3167.
[16] (a) T.K. Ganesan, J.R. Bosco Bharathy, A.I.Md. Sheriff, S. Rajagopal, Indian J. Chem. Sect. A 34 (1995) 522;
(b) R. Sevvel, S. Rajagopal, C. Srinivasan, N.I. Alhaji, A. Chellamani, J. Org. Chem. 65 (2000) 3334, and the references cited therein;
(c) J.B. Bharathy, T.K. Ganesan, A.I.Md. Sheriff, S. Rajagopal, Tetrahedron 53 (1997) 1131.
[17] (a) L. Zhang, P.A. Lay, J. Am. Chem. Soc. 118 (1996) 12624;
(b) G. Barr-David, M. Charara, R. Codd, R.P. Farrell, J.A. Irwin, P.A. Lay, R. Bramley, S. Brumby, J.-Y. Ji, G.R. Hanson, J. Chem. Soc., Faraday Trans. 91 (1995) 1207;
(c) P.A. Lay, A. Levina, J. Am. Chem. Soc. 120 (1998) 6704;
(d) M. Rizzotto, V. Moreno, S. Signorella, V. Daier, L.F. Sala, Polyhedron 19 (2000) 417;
(e) K.D. Sugden, K.E. Wetterhahn, J. Am. Chem. Soc. 118 (1996) 10811;
(f) A. Levina, A.M. Bailey, G. Champion, P.A. Lay, J. Am. Chem. Soc. 122 (2000) 6208;
(g) R. Codd, A. Levina, L. Zhang, T.W. Hambley, P.A. Lay, Inorg. Chem. 39 (2000) 990;
(h) R.P. Farrell, P.A. Lay, Comments Inorg. Chem. 13 (1992) 133.
[18] A. Levina, P.A. Lay, N.E. Dixon, Inorg. Chem. 39 (2000) 385.
[19] (a) R.N. Bose, B. Fonkeng, G. Barr-David, R.P. Farrell, R.J. Judd, P.A. Lay, D.F. Sangster, J. Am. Chem. Soc. 118 (1996) 7139;
(b) R.N. Bose, B.S. Fonkeng, S. Moghaddas, D. Stroup, Nucleic Acids Res. 26 (1998) 1588;
(c) R.N. Bose, B.S. Fonkeng, J. Chem. Soc., Chem. Commun. (1996) 2211;
(d) R.N. Bose, S. Moghaddas, P.A. Mazzer, L.P. Dudones, L. Joudah, D. Stroup, Nucleic Acids Res. 27 (1999) 2219.
[20] cf. A.K. Das, in: Proceedings of the Symposium on Modern Trends in Inorganic Chemistry—IX (MTIC-IX), Calcutta, 2001, p. P81.
[21] S.K. Mondal, Ph.D. Thesis, Visva Bharati University, West Bengal, India, 2001.
[22] A.I. Carbone, F.P. Cavasino, C. Sbriziolo, E. Pelizzetti, J. Phys. Chem. 89 (1985) 3578.
[23] (a) Kabir-ud-Din, A.M.A. Morshed, Z. Khan, Inorg. React. Mech. 3 (2002) 255.;
(b) Kabir-ud-Din, K. Hartani, S. Kumar, Z. Khan, Tenside Surf. Det. 38 (2001) 238.;
(c) Kabir-ud-Din, K. Hartani, Z. Khan, Colloids Surf. A: Physicochem. Eng. Aspects 193 (2001) 1.
[24] R. Swain, G.P. Panigrahi, Indian J. Chem. Sect. A 40 (2001) 1191.
[25] (a) J. Panda, G.P. Panigrahi, J. Indian Chem. Soc. 79 (2002) 58;
(b) G.P. Panigrahi, B.P. Shau, Int. J. Chem. Kinet. 25 (1993) 595.
[26] M. Matha, L.B.T. Sundari, K.C. Rajanna, P.K. Saiprakash, Int. J. Chem. Kinet. 28 (1996) 637.
[27] K.C. Rajanna, K.N. Reddy, U.U. Kumar, P.K. Saiprakash, Int. J. Chem. Kinet. 28 (1996) 153.
[28] R.D. Makote, C. Chatterjee, Indian J. Chem. Sect. A 37 (1998) 21.
[29] D.S. Gaur, J. Indian Chem. Soc. 74 (1997) 545.
[30] I.V. Berezin, K. Martinek, A.K. Yatsimirskii, Russ. Chem. Rev. 42 (1973) 787.
[31] (a) D. Myers, in: Surfaces, Interfaces and Colloids: Principles and Applications, VCH, New York, 1991, p. 299;
(b) C. Tanford, in: the Hydrophobic Effect: Formation of Micelles and Biological Membranes, second ed., Wiley, New York, 1980;
(c) cf. B. Simmons, V. Agarwal, G. McPherson, V. John, A. Bose, Langmuir 18 (2002) 8345;
(d) S. Kumar, V.K. Aswal, P.S. Goyal, Kabir-ud-Din, J. Chem. Soc., Faraday Trans. 94 (1998) 761;
(e) V.K. Aswal, P.S. Goyal, Phys. Rev. E 61 (2000) 2947;
(f) G. Montalvo, A. Khan, Langmuir 18 (2002) 8330;
(g) J.B. Berg, J.L. Tymoczko, L. Stryer, in: Biochemistry, fifth ed., W.H. Freeman and Company, New York, 2001, p. 323;
(h) A.S. Muresan, H. Diamant, K.Y.C. Lee, J. Am. Chem. Soc. 123 (2001) 6951;
(i) J.K. Harris, G.D. Rose, M.L. Bruening, Langmuir 18 (2002) 5337;
(j) cf. J.-Y. Im, D.-B. Kim, S.H. Lee, Y.-S. Lee, Langmuir 19 (2003) 6392;
(k) A. Filippov, G. Oradd, G. Lindblom, Langmuir 19 (2003) 6397;

(l) N. Tokutake, M. Uragami, S.L. Regen, Langmuir 19 (2003) 6363;
(m) cf. A. Kreimeyer, F. Andre, C. Gouyelte, T. Huynh-Dinh, Angew. Chem. Int. Ed. Engl. 37 (1998) 2853;
(n) cf. J.A. Boomer, H.D. Inerowicz, Z.-Y. Zhang, N. Bergstrand, K. Edwards, J.-M. Kim, D.H. Thompson, Langmuir 19 (2003) 6408.
[32] (a) cf. C.A. Bunton, F. Nome, F.H. Quina, L.S. Romsted, Acc. Chem. Res. 24 (1991) 357;
(b) E. Rodenas, E. Perez-Benito, J. Phys. Chem. 95 (1991) 4552;
(c) S.K. Hait, S.P. Moulik, Langmuir 18 (2002) 6736;
(d) E. Abuin, E. Lissi, R. Duarte, J.J. Silber, M.A. Biasutti, Langmuir 18 (2002) 8340;
(e) G.-W. Zhou, G.-Z. Li, W.-J. Chen, Langmuir 18 (2002) 4566.
[33] M. Valiente, E. Rodenas, J. Phys. Chem. 95 (1991) 3368.
[34] F.M. Menger, C.E. Portnoy, J. Am. Chem. Soc. 89 (1967) 4698.
[35] C.A. Bunton, G. Cerichelli, Int. J. Chem. Kinet. 12 (1980) 519.
[36] D. Piszkiewicz, J. Am. Chem. Soc. 99 (1977) 7695.
[37] Z. Khan, S.I. Ali, Z.A. Rafiquee, Kabir-ud-din, Indian J. Chem. Sect. A 36 (1997) 579.
[38] K.K. Ghosh, S.K. Kar, J. Indian Chem. Soc. 75 (1998) 39.
[39] G.P. Panigrahi, B.P. Sahu, J. Indian Chem. Soc. 68 (1991) 239.
[40] A.C. Dash, J. Prusti, J. Pradhan, P.K. Das, J. Chem. Soc., Faraday Trans. 86 (1990) 507.
[41] J.H. Espenson, Acc. Chem. Res. 3 (1970) 347.
[42] O.A. Babich, E.S. Gould, Inorg. Chem. 40 (2001) 5708.
[43] J.F. Perez-Benito, C. Arias, D. Lamrhari, J. Chem. Soc., Chem. Commun. (1992) 472.
[44] J.F. Perez-Benito, C. Arias, Can. J. Chem. 71 (1993) 649.
[45] (a) S.K. Chandra, S. Gelerinter, E.S. Gould, Inorg. Chem. 34 (1995) 4057;
(b) S. Meenakshisundaram, R. Vinothini, Croat. Chim. Acta. 76 (1) (2003) 75.
[46] (a) R. Codd, P.A. Lay, A. Levina, Inorg. Chem. 36 (1997) 5440;
(b) A. Levina, G.J. Foran, P.A. Lay, Chem. Commun. (1999) 2339.
[47] M.C. Ghosh, E.S. Gould, Inorg. Chem. 30 (1991) 491.
[48] M.C. Ghosh, E. Gelerinter, E.S. Gould, Inorg. Chem. 31 (1992) 702.
[49] F.H. Westheimer, Chem. Rev. 45 (1949) 419.
[50] (a) F. Hasan, J. Rocek, Tetrahedron 30 (1974) 21;
(b) J. Rocek, A.E. Radkowsky, J. Am. Chem. Soc. 95 (1973) 7123.
[51] Z. Khan, Kabir-ud-Din, M. Akram, J. Chem. Res. (S) (1998) 460.
[52] R.P. Farrell, P.A. Lay, A. Levina, I.A. Maxwell, R. Bramley, S. Brumby, J.-Y. Ji, Inorg. Chem. 37 (1998) 3159.
[53] S. Saraswat, V. Sharma, K.K. Banerji, Indian J. Chem. Sect. A 40 (2001) 583.
[54] I. Dave, V. Sharma, K.K. Banerji, Indian J. Chem. Sect. A 39 (2000) 728.
[55] K. Chowdhuri, P.K. Sharma, K.K. Banerji, Indian J. Chem. Sect. A 38 (1999) 325.
[56] S. Agarwal, K. Chowdhuri, K.K. Banerji, J. Org. Chem. 56 (1991) 5111.
[57] C.E. Harding, C.W. Mitchel, J. Devenyi, J. Chem. Educ. 77 (8) (2000) 1042.
[58] P.S.C. Rao, D. Suri, S. Kothari, K.K. Banerji, Int. J. Chem. Kinet. 30 (1998) 285.
[59] S.L. Scott, A. Bakac, J.H. Espenson, J. Am. Chem. Soc. 114 (1992) 4205.
[60] M.B. Smith, J. March, in: March's Advanced Organic Chemistry, fifth ed., Wiley, New York, 2001, p. 1517.
[61] S. Signorella, S. Garcia, L.F. Sala, Polyhedron 16 (1997) 701.
[62] M. Rizzotto, M.I. Frascaroli, S. Signorella, L.F. Sala, Polyhedron 15 (1996) 1517.
[63] S. Signorella, M. Rizzotto, V. Daier, M.I. Frascaroli, C. Palopoli, D. Martino, A. Bousseckso u, L.F. Sala, J. Chem. Soc., Dalton Trans. (1996) 1607.
[64] M. Rizzotto, S. Signorella, M.I. Frascaroli, V. Daier, L.F. Sala, J. Carbohydr. Chem. 14 (1995) 45.
[65] L.F. Sala, S. Signorella, M. Rizzotto, M.I. Frascaroli, F. Gandolfo, Can. J. Chem. 70 (1992) 2046.
[66] S.R. Signorella, M.I. Santoro, M.N. Mulero, L.F. Sala, Can. J. Chem. 72 (1994) 398.
[67] S. Garcia, S. Signorella, S. Acebal, E. Piaggio, L.F. Sala, Oxid. Commun. 16 (1993) 313.
[68] L.F. Sala, C. Palopoli, S. Signorella, Polyhedron 14 (1995) 1725.
[69] S. Signorella, V. Daier, S. Garcia, R. Cargnello, J.C. Gonzalez, M. Rizzotto, L.F. Sala, Carbohydr. Res. 316 (1999) 14.
[70] S. Singorella, R. Lafarga, V. Daier, L.F. Sala, Carbohydr. Res. 324 (2) (2000) 127.
[71] S. Signorella, M.I. Frascaroli, S. Garcia, M. Santoro, J.C. Gonzalez, C. Palopoli, V. Daier, N. Casado, L.F. Sala, J. Chem. Soc., Dalton Trans. (2000) 1617.
[72] S. Signorella, S. Garcia, L.F. Sala, J. Chem. Educ. 76 (1999) 405.
[73] V. Daier, S. Signorella, M. Rizzotto, M.I. Frascaroli, C. Palopoli, C. Brondino, J.M. Salas-Peregrin, L.F. Sala, Can. J. Chem. 77 (1999) 57.
[74] M. Rizzotto, A. Levina, M. Santoro, S. Garcia, M.I. Frascaroli, S. Signorella, L.F. Sala, P.A. Lay, J. Chem. Soc., Dalton Trans. (2002) 3206.
[75] (a) C. Palopoli, S. Signorella, L.F. Sala, New J. Chem. 21 (1997) 343;
(b) V. Roldan, V. Daier, B. Goodman, M. Santoro, J.C. Gonzalez, N. Calisto, S. Signorella, L.F. Sala, Helv. Chim. Acta 83 (2000) 3211.
[76] S. Signorella, M. Santoro, C. Palopoli, C. Brondino, J.M. Salas-Peregrin, M. Quiroz, L.F. Sala, Polyhedron 17 (1998) 2739.
[77] D.M. Stearns, K.E. Wetterhahn, Chem. Res. Toxicol. 7 (1994) 219.
[78] J.F. Perez-Benito, D. Lamhari, C. Arias, Can. J. Chem. 72 (1994) 1637.
[79] Kabir-ud-Din, K. Hartani, Z. Khan, Transition Met. Chem. 25 (4) (2000) 478.
[80] Z. Khan, Kabir-ud-Din, Transition Met. Chem. 26 (2001) 672.
[81] (a) Z. Khan, Kabir-ud-Din, Indian J. Chem. Sect. A 38 (1999) 361;
(b) Z. Khan, Kabir-ud-Din, Transition Met. Chem. 26 (2001) 481.
[82] C. Srinivasan, A. Chellamani, S. Rajagopal, J. Org. Chem. 50 (1985) 1201.
[83] G.S. Gokavi, Indian J. Chem. Sect. A 40 (2001) 307.
[84] A. Kortenkamp, M. Casadevall, S.P. Faux, A. Jenner, R.O.J. Shayer, N. Woodbridge, P. O'Brien, Arch. Biochem. Biophys. 329 (1996) 199.
[85] L. Zhang, P.A. Lay, Aust. J. Chem. 53 (2000) 7.
[86] D.W.J. Kwong, D.E. Pennington, Inorg. Chem. 23 (1984) 2528.
[87] B.L. Hiran, S.L. Chaplot, V. Joshi, G. Chaturvedi, Kinet. Catal. 43 (5) (2002) 657.
[88] H.A. Headlam, C.L. Weeks, P. Turner, T.W. Hambley, P.A. Lay, Inorg. Chem. 40 (2001) 5097.
[89] H.A. Headlam, P.A. Lay, Inorg. Chem. 40 (2001) 78.
[90] Z. Khan, Kabir-ud-Din, Indian J. Chem. Sect. A 40 (2001) 528.
[91] G.P. Haight, G.M. Jursich, M.T. Kelso, P.J. Merrill, Inorg. Chem. 24 (1985) 2740.
[92] S.P. Kaiwar, C.P. Rao, Chem. Biol. Interact. 95 (1995) 89.
[93] C.P. Rao, S.P. Kaiwar, Carbohydr. Res. 244 (1993) 15.
[94] C.P. Rao, S.P. Kaiwar, Carbohydr. Res. 237 (1992) 195.
[95] (a) R.N. Bose, S. Moghaddas, E. Gelerinter, Inorg. Chem. 31 (1992) 1987;
(b) S. Moghaddas, E. Gelerinter, R.N. Bose, J. Inorg. Biochem. 57 (1995) 135.
[96] S.L. Brauer, A.S. Hneihen, J.S. McBride, K.E. Wetterhahn, Inorg. Chem. 35 (1996) 373.
[97] P.A. Lay, A. Levina, Inorg. Chem. 35 (1996) 7709.
[98] P. O'Brien, G. Wang, P.B. Wyatt, Polyhedron 11 (1992) 3211.
[99] J.F. Perez-Benito, D. Lamarhari, C. Arias, J. Phys. Chem. 98 (1994) 12621.

[100] X. Shi, M. Ding, J. Ye, S. Wang, S.S. Leonard, L. Zang, V. Castranova, V. Vallyathan, A. Chiu, N. Dalal, K. Liu, J. Inorg. Biochem. 75 (1999) 37.
[101] P. O'Brien, N. Woodbridge, Polyhedron 16 (1997) 2897.
[102] J.F. Perez-Benito, N. Saiz, E. Amat, J. Mol. Catal. A 135 (1998) 1.
[103] J.F. Perez-Benito, C. Arias, D. Lamrhari, A. Anhari, Int. J. Chem. Kinet. 26 (1994) 587.
[104] J.F. Perez-Benito, C. Arias, D. Lamrhari, New J. Chem. 18 (1994) 663.
[105] D.A. Dixon, T.P. Dasgupta, N.P. Sadler, J. Chem. Soc., Dalton Trans. (1995) 2267.
[106] K.B. Wiberg, G. Szeimies, J. Am. Chem. Soc. 96 (1974) 1889, and the references cited therein.
[107] R.E. Hintze, J. Rocek, J. Am. Chem. Soc. 99 (1977) 132.
[108] D.A. Dixon, T.P. Dasgupta, N.P. Sadler, J. Chem. Soc., Dalton Trans. (1997) 1903.
[109] D.A. Dixon, N.P. Sadler, T.P. Dasgupta, J. Chem. Soc., Dalton Trans. (1993) 3489.
[110] J.F. Perez-Benito, C. Arias, Int. J. Chem. Kinet. 25 (1993) 221.
[111] I. Rao, S.K. Misra, P.D. Sarma, Trans. Met. Chem. 17 (1992) 449.
[112] P. O'Brien, N. Woodbridge, Polyhedron 16 (1997) 2081.
[113] S.A. Kazmi, M.U. Rahaman, J. Chem. Soc. Pak. 19 (1997) 201.
[114] B. Sankararaj, S. Rajagopal, K. Pitchumani, Indian J. Chem. Sect. A 34 (1995) 440.
[115] T.K. Ganesan, S. Rajagopal, J.B. Bharathy, Tetrahedron 56 (2000) 5885.
[116] H. Lund, K. Dassbjerg, T. Lund, S.U. Pedersen, Acc. Chem. Res. 28 (1995) 313.
[117] G.P. Haight, Jr. Tracy, J. Huang, B.Z. Shakhashiri, J. Inorg. Nucl. Chem. 33 (1971) 2169.
[118] M.A. Olatunji, G.A. Ayoko, Polyhedron 7 (1988) 11.
[119] D.D. Virkar, G.S. Gokavi, Indian J. Chem. 38A (1999) 1268.
[120] (a) F. Hasan, J. Rocek, J. Am. Chem. Soc. 96 (1974) 534;
(b) S. Ramesh, S.N. Mahapatro, J.H. Liu, J. Rocek, J. Am. Chem. Soc. 103 (1981) 5172.
[121] A.K. Das, A. Roy, B. Saha, M. Das, J. Chem. Res. (S) (2001) 62.
[122] A.K. Das, Oxid. Commun. 24 (2001) 321, and the references cited therein.
[123] A.K. Das, A. Roy, B. Saha, M. Das. J. Chem. Res. (S) (2001) 334.
[124] S. Signorella, S. Garcia, L.F. Sala, Polyhedron 11 (1992) 1391.
[125] S. Meenakshisundaram, R. Sockalingam, Bull. Chem. Soc. Jpn. 74 (2001) 1043.
[126] R.T. Sabapathy Mohan, M. Gopalakrishnan, M. Sekar, Tetrahedron 50 (1994) 10933.
[127] E. Perez-Benito, E. Rodenas, Langmuir 7 (1991) 232.
[128] E. Rodenas, E. Perez-Benito, J. Phys. Chem. 95 (1991) 9496.
[129] A.K. Das, A. Roy, S.K. Mondal, G. Mukherjee, React. Kinet. Catal. Lett. 73 (2001) 257.
[130] A.K. Das, D. Kar, S.K. Mondal, Inorg. React. Mech. 3 (2001) 83.
[131] A.K. Das, A. Roy, B. Saha, Trans. Met. Chem. 26 (2001) 630.
[132] B. Saha, M. Das, A.K. Das, J. Chem. Res. (S), in press.
[133] S.K. Mondal, M. Das, D. Kar, A.K. Das, Indian J. Chem. Sect. A 40 (2001) 352.
[134] S.K. Sahu, G.P. Panigrahi, J. Indian Chem. Soc. 73 (1996) 576.
[135] G.P. Panigrahi, S.K. Mishra, J. Chem. Res. (S) 180 (1990).
[136] E. Perez-Benito, E. Rodenas, Trans. Met. Chem. 18 (1993) 329.
[137] A.K. Das, S.K. Mondal, D. Kar, M. Das, Inorg. React. Mech. 3 (2001) 63.
[138] A.K. Das, A. Roy, B. Saha, R.K. Mohanty, M. Das, J. Phys. Org. Chem. 14 (2001) 333.
[139] B. Saha, M. Das, R.K. Mohanty, A.K. Das, J. Chin. Chem. Soc., in press.
[140] Z.A. Rafiquee, R.A. Shah, Kabir-ud-Din, Z. Khan, Int. J. Chem. Kinet. 29 (1997) 131 and the references cited therein.
[141] S. Mishra, A.K. Panigrahi, B.K. Sinha, J. Indian Chem. Soc. 74 (1997) 408.
[142] G.P. Panigrahi, S.K. Mishra, J. Mol. Catal. 81 (1993) 349.
[143] G.P. Panigrahi, S.K. Sahu, Indian J. Chem. Sect. A 35 (1996) 660.
[144] G.P. Panigrahi, S.K. Mishra, Indian J. Chem. Sect. A 32 (1993) 956.
[145] G.P. Panigrahi, S.K. Mishra, Indian J. Chem. Sect. A 31 (1992) 710.
[146] A.K. Das, S.K. Mondal, D. Kar, A. Roy, M. Das, in: Proceedings of the Symposium on Modern Trends in Inorganic Chemistry—VIII (MTIC-VIII), Bangalore, 2000, p. 19.
[147] A.K. Das, Proceeding of the International Conference on Chemistry and 36th Annual Convention of Chemists, Indian Chemical Society, 1999, p. B30.
[148] (a) A.K. Das, Inorg. React. Mech. 1 (1999) 161;
(b) A.K. Das, D.Sc. Thesis, Visva Bharati University, West Bengal, India.
[149] Kabir-ud-Din, K. Hartani, Z. Khan, Int. J. Chem. Kinet. 33 (2001) 377.
[150] A.K. Das, S.K. Mondal, D. Kar, M. Das, J. Chem. Res. (S) (1998) 574.
[151] A.K. Das, S.K. Mondal, D. Kar, M. Das, Int. J. Chem. Kinet. 33 (2001) 173.
[152] S. Oae, Y. Uchida, Acc. Chem. Res. 24 (1991) 202.
[153] N.C. Sarada, I.A.K. Reddy, J. Indian Chem. Soc. 70 (1993) 35.
[154] Kabir-ud-Din, M. Akram, Z. Khan, Inorg. React. Mech. 4 (2002) 187.
[155] J. Skrzewski, E. Cichacz, Bull. Chem. Soc. Jpn. 57 (1984) 271.