SHORT PAPER

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Micellar effects on the reaction of Cr(VI) oxidation of hexitols in the presence and absence of picolinic acid in aqueous acid media.

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In aqueous acidic media, picolinic acid (PA) promoted Cr^{VI}-oxidation of the hexitols to the respective aldohexoses goes on, along with a slower uncatalysed path; the anionic surfactant (SDS) accelerates the process while the cationic surfactant (CPC) retards the reaction.

Keywords: picolinic acid, Cr(VI)oxidation, hexitols

Among the different types of chelating agents[1] such as 2,2′-bypiridine, 1,10-phenanthroline, aminopolycarboxylic acids, oxalic acids, etc, which act as catalysts in Cr^{VI} oxidation, picolinic acid (PA) is unique.[2] PA is not cooxidised but it is gradually lost due to formation of a Cr^{III}–PA complex. PA can efficiently catalyse the Cr^{VI}-oxidation of different types of substrates including the monohydric alcohols. The present paper describes micellar effects on Cr^{VI}-oxidation of two representative hexitols in the presence of PA. The micellar effects have been studied to substantiate the proposed reaction mechanisms and to test the applicability of the Piszkiewicz cooperative model[3] to explain the micellar effect.

Under the experimental conditions, $[\text{hexitol}]_T >> [Cr^{VI}]_T$ and $[PA]_T >> [Cr^{VI}]_T$ (subscript T stands for the total concentration) hexitols are oxidised to the corresponding aldohexoses which are detected and confirmed by spot tests.[4] The overall stoichiometry of the reaction may be represented as (where R = $HOCH_2(CHOH)_4$—):

$$2RCH_2OH + 3HCrO_4^- + 17H^+ \rightarrow 2RCHO + 3Cr^{III} + 12H_2O \quad (1)$$

The rate of disappearance shows a first-order dependence on $[Cr^{VI}]_T$ and the pseudo-first-order rate constants (k_{obs}) were evaluated from the plot of $\log[Cr^{VI}]_t$ *vs.* time (t) as usual. From the dependence of [PA] (*i.e.* k_{obs} *vs* $[PA]_T$ plot, *see* Fig. 1), it is observed that both the catalysed (*i.e.* $k_{obs(c)}$) and uncatalysed (*i.e.* $k_{obs(u)}$) paths go on simultaneously.

$$k_{obs(T)} = k_{obs(u)} + k_{obs(c)} = k_{obs(u)} + k_{cat}[PA]_T \quad (2)$$

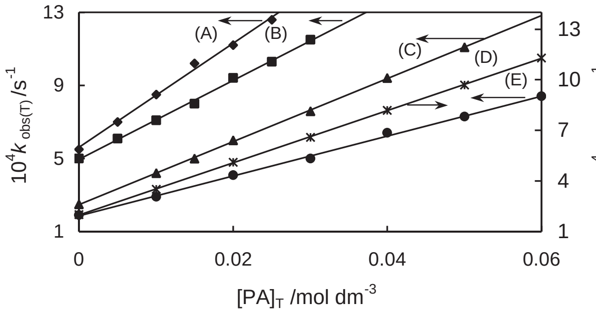

Fig. 1 Dependence of k_{obs} on $[PA]_T$ for the Cr^{VI} oxidation of D-mannitol. $[Cr^{VI}]$ = 5x 10^{-4} mol dm^{-3}, $[H_2SO_4]$ = 1.0 mol dm^{-3}, [D-mannitol] = 0.01 mol dm^{-3}, A (35°C), B (45°C, $[CPC]_T$ = 8x10^{-3} mol dm^{-3}), C(25°C), D (20°C, $[HClO_4]$ = 0.45 mol dm^{-3}, [D-mannitol] = 7.5x10^{-3} mol dm^{-3}), E (35°C, $[CPC]_T$ = 8x10^{-3} mol dm^{-3}).

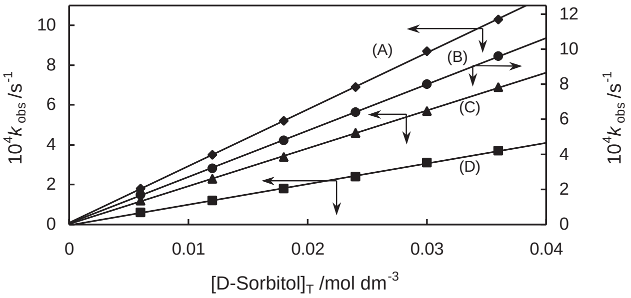

Fig. 2 Dependence of k_{obs} on $[\text{D-sorbitol}]_T$ for the Cr^{VI} oxidation of D-sorbitol. $[Cr^{VI}]_T$ = 4x10^{-4} mol dm^{-3}, $[H_2SO_4]$ = 0.5 mol dm^{-3}, 25°C. A ($[PA]_T$ = 4x10^{-3} mol dm^{-3}); B ($[SDS]_T$ = 0.02 mol dm^{-3}), C (no surfactant, no catalyst), D ($[CPC]_T$ = 4x10^{-3} mol dm^{-3}).

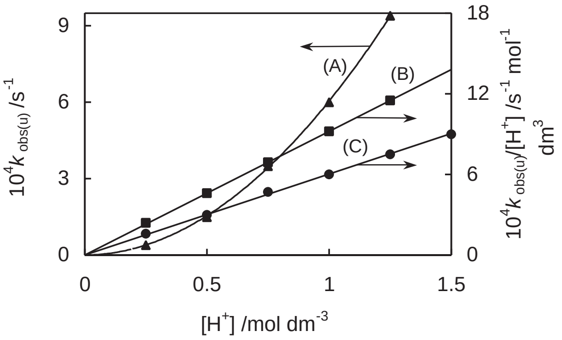

Fig. 3 Dependence of k_{obs} on $[H^+]$ for the Cr^{VI} oxidation of D-sorbitol at 20°C. $[HClO_4]$ + $[NaClO_4]$ = I = 1.5 mol dm^{-3}. A (no surfactant), B ($[SDS]_T$ = 0.02 mol dm^{-3}), C (no surfactant).

The activation parameters for k_{cat} (Table 1) in aqueous H_2SO_4 media are $\Delta H^{\neq}$ = 36 ± 1.5 kJ mol^{-1}, $\Delta S^{\neq}$ = -160 + 8 J K^{-1} mol^{-1} for D-mannitol; $\Delta H^{\neq}$ = 48 ± 2.5 kJ mol^{-1}, $\Delta S^{\neq}$ = –122 ± 10 JK^{-1} mol^{-1} for D-sorbitol. The activation parameters were calculated by using the Eyring equation as usual from the k_{cat} values at three to four different temperatures in the range 20 to 45 °C. The $k_{obs(u)}$ values determined independently agree satisfactorily with those obtained from the intercepts of the k_{obs} *vs* $[PA]_T$ plots. From the plot of k_{obs} *vs.* $[S]_T$ (*see* Fig. 2), the dependence on $[S]_T$ is expressed as follows:

$$k_{obs(u)} = k_{s(u)}[S]_T \text{ and } k_{obs(c)} = k_{obs(T)} – k_{obs(u)} = k_{s(c)}[S]_T \quad (3)$$

The acid dependence patterns for the uncatalysed and catalysed paths are different and the experimental findings (*see* Fig. 3) conform to:

$$k_{obs(u)} = k_{H(u)}[H^+]^2 \text{ and } k_{obs(c)} = k_{obs(T)} - k_{obs(u)} = k_{H(c)}[H^+]^0 \quad (4)$$

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Kinetic parameters and some representative rate constants for the Cr^{VI} oxidation of D-mannitol and D-sorbitol in the presence and absence of picolinic acid (PA).

Temp. /°C	$10^4k_{obs(u)(w)}$ ^{a}/ s^{-1}	$10^2k_{cat(w)}$ ^{a} /dm^3 mol^{-1} s^{-1}	$10^2k_{cat(CPC)}$ ^{b} /dm^3 mol^{-1} s^{-1}	$k_{eff(w)}$ ^{c}	$10^2k_{s(u)(w)}$ ^{d} /dm^3 mol^{-1} s^{-1}	$10^2k_{s(c)(w)}$ ^{d} /dm^3 mol^{-1} s^{-1}	$10^2k_{s(u)(CPC)}$ ^{d} /dm^3 mol^{-1} s^{-1}	$10^2k_{s(c)(CPC)}$ ^{d} /dm^3 mol^{-1} s^{-1}	$10^2k_{s(u)(SDS)}$ ^{d} /dm^3 mol^{-1} s^{-1}
in aqueous H_2SO_4 medium									
35°C (for D-Mannitol)	5.50±0.20	2.80±0.10	1.14±0.08	1.04	4.96±0.07	2.04±0.05	1.59±0.05	1.54±0.04	6.33±0.15
25°C (for D-Sorbitol	1.20±0.10	1.22±0.10	0.50±0.04	2.08	1.92±0.06	0.98±0.04	1.00±0.03	0.80±0.03	2.70±0.003
in aqueous HClO4 media									
20°C (for D-Mannitol	2.00±0.01	1.55±0.15		1.55					
25°C (for D-Mannitol					3.00±0.10	1.30±0.02			
25°C (for D-Sorbitol	1.40±0.10	1.47±0.10	0.60±0.06	2.07	2.70±0.15	1.40±0.04	1.50±0.05	1.20±0.05	3.80±0.10

Subscripts: (u) for uncatalysed path; (c) for PA-catalysed path, (w) for the value in absence of surfactant; (CPC) or (SDS) for the value in the presence of the respective surfactant)

For D-mannitol in aqueous H_2SO_4 media:

[a] $[Cr^{VI}]_T = 5x10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[S]_T = 1x10^{-2}$ mol dm^{-3}, $[PA]_T = (0 – 0.055)$ mol dm^{-3}.

[b] Same as in (a), $[CPC]_T = 8x10^{-3}$ mol dm^{-3}, $[PA]_T = (0 – 0.08)$ mol dm^{-3}.

[c] Same as in (a) and $k_{eff(w)} = [k_{obs(T)} – k_{obs(u)}]/k_{obs(u)}$ and k_{eff} calculated at $[PA]_T = 0.02$ mol dm^{-3}.

[d] $[Cr^{VI}]_T = 5x10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[S]_T = (0.005 – 0.075)$ mol dm^{-3}, $[CPC]_T = 8x10^{-3}$ mol dm^{-3}, $[PA]_T = 5x10^{-3}$ mol dm^{-3}, $[SDS]_T = 4x10^{-3}$ mol dm^{-3}.

For D-sorbitol in aqueous H_2SO_4 media:

[a] $[Cr^{VI}]_T = 4x10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[S]_T = 6x10^{-3}$ mol dm^{-3}, $[PA]_T = (0 – 0.09)$ mol dm^{-3}.

[b] Same as in (a) $[CPC]_T = 4x10^{-3}$ mol dm^{-3}, $[PA]_T = (0 – 0.12)$ mol dm^{-3}.

[c] k_{eff} calculated at $[PA]_T = 0.02$ mol dm^{-3} and other conditions as in (a).

[d] $[Cr^{VI}]_T = 4x10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[SDS]_T = 2x10^{-2}$ mol dm^{-3}, $[CPC]_T = 4x10^{-3}$ mol dm^{-3}, $[PA]_T = 4x10^{-3}$ mol dm^{-3}, $[S]_T = (0.005 – 0.036)$ mol dm^{-3}.

For D-mannitol in aqueous $HClO_4$ media:

[a] $[Cr^{VI}]_T = 5x10^{-4}$ mol dm^{-3}, $[HClO_4] = 0.45$ mol dm^{-3}, $[S]_T = 7.5 \times 10^{-3}$ mol dm^{-3}, $[PA]_T = (0 – 0.07)$ mol dm^{-3}.

[c] k_{eff} calculated at $[PA]_T = 0.02$ mol dm^{-3} and other conditions as in (a).

[d] $[Cr^{VI}]_T = 5x10^{-4}$ mol dm^{-3}, $[HClO_4] = 0.45$ mol dm^{-3}, $[S]_T = (0.005 – 0.04)$ mol dm^{-3}, $[PA]_T = 5x10^{-3}$mol dm^{-3}.

For D-sorbitol in aqueous $HClO_4$ media:

[a] $[Cr^{VI}]_T = 4x10^{-4}$ mol dm^{-3}, $[HClO_4] = 0.5$ mol dm^{-3}, $[S]_T = 6.0x10^{-3}$ mol dm^{-3}, $[PA]_T = (0 – 0.09)$ mol dm^{-3} dm^{-3}, $I = 1.0$ mol dm^{-3}.

[b] Same as in (a) ,$[PA]_T = (0 – 0.1)$ mol dm^{-3}, $[CPC]_T = 4 \times 10^{-3}$ mol dm^{-3}.

[c] k_{eff} calculated at $[PA]_T = 0.02$ mol dm^{-3} and other conditions as in (a).

[d] $[Cr^{VI}]_T = 4x10^{-4}$ mol dm^{-3}, $[HClO_4] = 0.5$ mol dm^{-3}, $[SDS]_T = 2x10^{-2}$ mol dm^{-3}, $[PA]_T = 4x10^{-3}$mol dm^{-3}, $I = 1.0$ mol dm^{-3}.

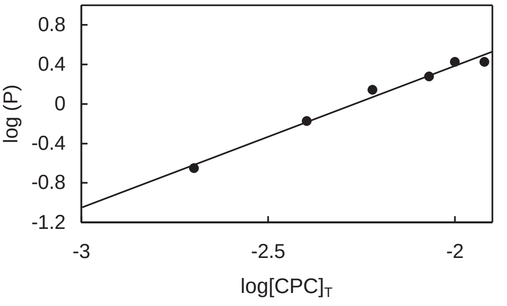


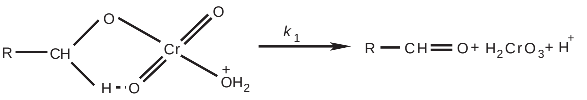
Fig. 4 Applicability of Piszkiewicz model (*i.e.* plot of log(P) *vs.* $log[CPC]_T$ to explain the micellar effect on $k_{obs(u)}$ for the Cr^{VI} oxidation of D-mannitol in the presence of cetylpyridinium chloride in aqueous H_2SO_4 media. $[Cr^{VI}]_T = 5x10^{-4}$ mol dm^{-3}; $[H_2SO_4] = 1.0$ mol dm^{-3}; $[D\text{-mannitol}]_T = 0.01$ mol dm^{-3} at 35°C. P is defined as : $P = (k_w – k_{obs(u)})/(k_{obs(u)} – k_m)$; $k_m \sim 0$.

For D-mannitol, $10^4k_{H(u)}/dm^6\ mol^{-2}\ s^{-1}$ (20 °C) is 7.0 ± 0.15 and it increases to 11.5 ± 0.25 in the presence of $[SDS]_T = 3x10^{-2}$ mol dm^{-3} (SDS = sodium dodecyl sulfate) for $[Cr^{VI}]_T = 5x10^{-4}$ mol dm^{-3}, $[D\text{-mannitol}]_T = 1x10^{-2}$ mol dm^{-3}, $[H^+] = (0 – 1.50)$ mol dm^{-3}, $I = 1.5$ mol dm^{-3}. Thus the observed rate laws can be expressed as follows:

$$k_{obs(u)} = a[S]_T[H^+]^2 \text{ and } k_{obs(c)} = k_{obs(T)} – k_{obs(u)} = b[S]_T[H^+]^0[PA]_T \quad (5)$$

$$RCH_2OH + HCrO_4^- + H^+ \rightleftharpoons R–CH_2–O–CrO_2–OH\ (\mathbf{1}) + H_2O,\ K_1 \quad (6)$$

$$\mathbf{1} + H_3O^+ \rightleftharpoons R–CH_2–O–CrO_2–OH_2^+\ (\mathbf{2}) + H_2O,\ K_2 \quad (7)$$



(2)

(8)

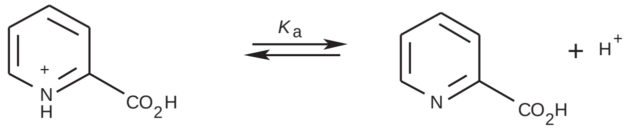
Scheme 1 Chromic acid oxidation of hexitol
[R = HOCH2(CHOH)4—].

The findings can be explained by considering the proposed mechanism (Schemes 1 and 2). Within the cyclic transition state (**2** in Scheme 1), Cr^{VI} is reduced to $Cr^{IV.}$ Then Cr^{IV} may be further reduced[5] to Cr^{III} through the partial oxidation of hexitol or Cr^{IV} may be oxidised to Cr^V by Cr^{VI}. Then Cr^V may oxidise the substrate as a 2*e*-oxidant. Alternatively, according to Perez-Benito *et al.*,[6] Cr^{IV} is reduced to Cr^{II} through hydride transfer from the substrate followed by the rapid oxidation of Cr^{II} by Cr^{VI} to Cr^{III}. The acrylonitrile polymerisation may be explained either by free-radical formation (1–*e* oxidation by Cr^{IV}) or by carbocation[7] (produced through hydride transfer from substrate to Cr^{IV}) formation.

Scheme 1 leads to the following rate law (assuming K_1 and K_2 to be quite small) under the conditions. The factor 2/3 comes from the consideration of the stoichiometry of the overall reaction (Eqn (1)).

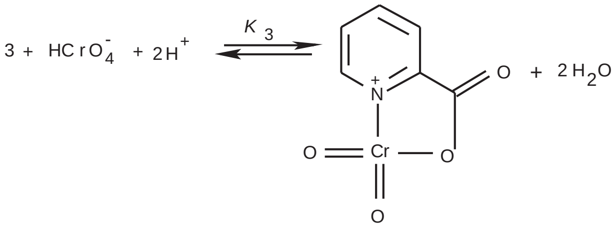
$$k_{obs(u)} = (2/3)K_1K_2k_1[S]_T[H^+]^2 = k_{s(u)}[S]_T = k_{H(u)}[H^+]^2 \qquad (9)$$

Scheme 2 leads to the following rate law under the steady-state condition of the proposed ternary complex (**5**).



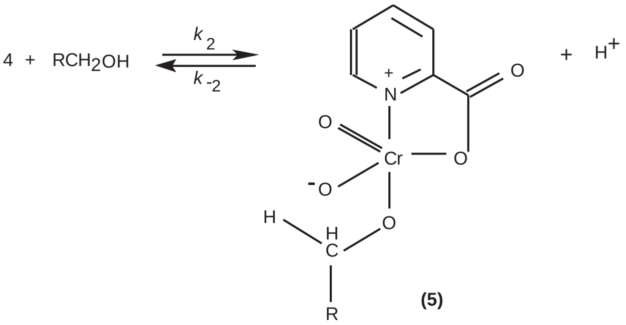
(3)

(10)

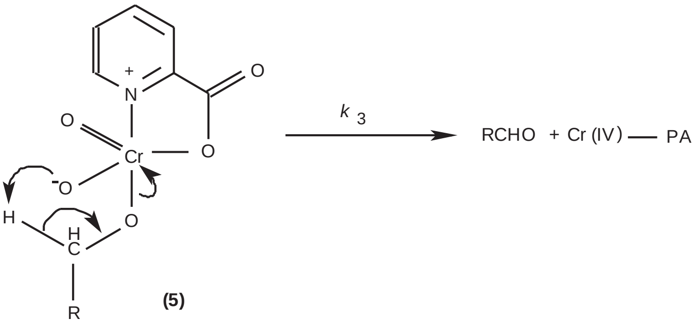


(4)

(11)



(12)



(13)

$$k_{obs(c)} = (2/3)K_aK_3k_2k_3[PA]_T[S]_T[H^+]^2/ \{(k_{-2}[H^+] + k_3)([H^+] + K_a)\} \qquad (14)$$

The rate law is obtained from the relation $-d[HCrO_4]/dt = k_3[\mathbf{5}]_T$ under the steady-state concentration of the species **5**, assuming $[S]_T = [S]$ and $[PA]_T = [PA] + [PAH^+]$ when $[S]_T >> [PA]_T >> [Cr^{VI}]_T$, *i.e.*

$$d[\mathbf{5}]/dt = 0 = k_2[S][\mathbf{4}] - (k_{-2}[H^+] + k_3)[\mathbf{5}];\ \text{or, } [\mathbf{5}] = k_2[S]_T[\mathbf{4}]/(k_{-2}[H^+] + k_3) \qquad (15)$$

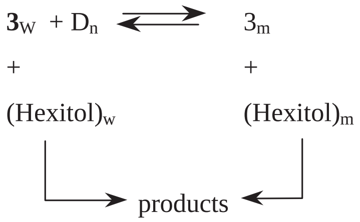
$$[\mathbf{4}] = K_3[PA][HCrO_4^-][H^+]^2 = K_aK_3[HCrO_4^-][H^+]^2[PA]_T/(K_a + [H^+]) \qquad (16)$$

Under the conditions, $[H^+] = (0.25 - 1.5)$ mol dm^{-3} $>> K_a$ (= 0.025 mol dm^{-3})[8] and $k_{-2}[H^+] >> k_3$, Eqn (14) is reduced to Eqn (17) which is in good agreement with the experimental findings. Similar observations have been noted for the substrates like methanol[2] and formic acid[9].

$$k_{obs(c)} = (2/3)K_aK_3k_2k_3[PA]_T[S]_T/k_{-2} = k_{cat}[PA]_T = k_{s(c)}[S]_T \qquad (17)$$

The catalytic efficiency of PA arises from the enhancement of the reduction potentials of the couples Cr^{VI}/Cr^{IV} and Cr^{VI}/Cr^{III} through the stabilisation of Cr^{IV} and Cr^{III} respectively.

The reactions (both catalysed and uncatalysed paths) are catalysed by SDS (sodium dodecyl sulfate, an anionic surfactant) and inhibited by CPC (*N*-cetylpyridinium chloride, a cationic surfactant). The specific rate constants in the presence of surfactants have been compared (Table 1) with those in the absence of surfactants. To circumvent the solubility problem, different acids $HClO_4$ and H_2SO_4 have been used for the anionic (SDS) and cataionic (CPC) surfactants. The observations can be explained by considering the pseudo-phase ion exchange (PIE) model[10] which considers the micellar and aqueous phases as two distinct phases. The reactants are considered to be distributed between these phases. In the uncatalysed path, the substrate and the kinetically active species H_2CrO_4 are preferably partitioned in the Stern layer of the micellar phase. In other words, it may be considered that the neutral Cr^{VI}-substrate ester (**2**) is concentrated in the Stern layer of the micellar phase. For the redox decomposition of the ester, it requires protonation.



Scheme 3 Distribution of reactants in the presence of PA for chromic acid oxidation of hexitols.

The approach of a proton to the anionic micellar head groups is electrostatically favoured, but it is disfavoured in the presence of cationic micellar head groups. This is why, in the presence of CPC, the reaction is restricted to the aqueous phase only where the concentration of the reactants is depleted due to preferential partitioning in the micellar phase. On the other hand, in the presence of SDS, the reaction goes on in both the phases and the process is favoured in the micellar phase where the reactants are preferably concentrated. This explains the catalysis by SDS and inhibition by CPC.

In the presence of PA, the positively charged Cr^{VI}–PA complex (**4**) and substrate are preferably accumulated in the anionic micellar phase of SDS and this explains the origin of the catalysis (Scheme 3).[11] In fact, in the presence of SDS, the reaction simultaneously goes on in both in the micellar phase and aqueous phase and the rate is accelerated in the micellar phase because of preferential accumulation of the reactants in the micellar phase. In the presence of CPC, although the substrate is partitioned in the micellar phase, the approach of the active oxidant Cr^{VI}–PA complex (which is positively charged) is repelled. Thus in the presence of CPC, the reaction is restricted to the aqueous phase which is depleted in the concentration of the substrate. This leads to rate retardation.

The slope of the plot of k_{obs} (for both the catalysed and uncatalysed paths) *vs* $[CPC]_T$ shows a continuous decrease and finally it levels off at higher $[CPC]_T$. A similar observation has been noted by Bunton and Cerichelli[12] in the oxidation of ferrocene by ferric salts in the presence of cetyltrimethylammonium bromide (CTAB). The rate data were subjected to the Piszkiewicz cooperative model[3] which gives the following relationship.

$$\log[(k_{obs} - k_w)/(k_m - k_{obs})] = \log(P) = n\log[CPC]_T - \log K_D \qquad (18)$$

Here K_D gives the dissociation constant of micellised surfactant back to its components, n is the index of cooperativity, $[CPC]_T$ gives the total surfactant concentration. Originally, the above equation was developed for micelle catalysed reactions showing a maximum rate followed by inhibition. However, it has been applied by many workers[13] in cases where the surfactant shows a monotonic effect as in the present case. Here k_w is the k_{obs} without any CPC and k_m is taken as zero for the CPC inhibited reaction. Fig. 1 gives the following results $n = 1.5$, $\log K_D = -3.42$ (indicating the interaction is fairly high) and $\log[CPC]_{50} = (= -2.28)$ representing the concentration of the required surfactant for half the maximum inhibition. The estimated $\log[CPC]_{50}$ values nicely agree with those experimentally observed. The small values of n (far less than the aggregation number 20 – 100 of the surfactant micelles)[3] indicate the existence of catalytically productive submicellar aggregates.

Experimental

PA (m.p. 136 °C)(Fluka) was used after recrystallisation from methanol. Hexitols and all other chemicals used were of analytical grade or general reagent grade purified by standard procedures. Progress of the reaction was monitored by following the rate of disappearance of Cr^{VI}. The concentration of Cr^{VI} at different time intervals was measured by a titrimetric quenching technique using excess of standard Mohr's solution and the unreacted Fe^{II} was estimated by a standard Ce^{IV} solution using ferroin indicator[9]. The pseudo-first-order rate constants were calculated from the slopes of the plots of $\log[Cr^{VI}]_t$ *vs*. time (t) which were linear at least up to 3 half-lives.

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