

Effect of sodium lauryl sulphate micelle in the oxidation of *dl*-mandelic acid by Cr(VI)

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dl-Mandelic acid on oxidation by Cr(VI) in the absence and presence of sodium lauryl sulphate (NaLS) follows a route conforming to Michaelis-Menten kinetics. Rate data in the presence of $[H^+]$ show an acid dependent and acid independent path. Entropy of activation is found to be negative. Rate of oxidation is mildly enhanced in the presence of increasing concentration of NaLS upto the CMC value of NaLS beyond which rate decreases. An attempt has been made to rationalise the observations.

Investigation of reaction mechanism in organised assemblies is being increasingly carried out in view of the interest derived from realisation that many biochemical processes proceed in a microheterogeneous system which contains an aqueous and a lipophilic moiety¹. Among the biochemical functions, the redox processes represent reactions of primary importance². Electron-transfer processes in micellar systems can be considered as models to get insight into electron transport occurring in biological phenomena³. In the light of this consideration, we have undertaken oxidation of organic substrates by Cr(VI) in the presence of sodium lauryl sulphate (NaLS) micelles⁴⁻⁷. In order to throw further light into the electron transfer reactions of Cr(VI) in the presence of NaLS micelle, we have extended our study to the oxidation of the *dl*-mandelic acid by Cr(VI) in presence of NaLS.

Oxidation of hydroxy acids⁸⁻¹⁰ by Cr(VI) has been frequently studied kinetically to unravel the pathways operating in reduction of Cr(VI) and has constituted a model system for demonstration of three electron transfer process in oxidation by Cr(VI). We have undertaken studies of catalysis by the surfactant sodium lauryl sulphate (NaLS) in the oxidations by Cr(VI) of substrates containing more than one functional group with a view to obtaining evidences of the involvement of both functional groups in the oxidation in the presence of sodium lauryl sulphate. In this regard we have already reported the oxidation of lactic acid⁷ and *dl*-tartaric acid¹¹ by Cr(VI) in the presence of sodium lauryl sulphate. Although complex rate laws in which both first and second order rate depend-

ence in the hydroxy acids had been reported⁹, no such dependence was observed by us under the present experimental conditions. To confirm the findings we have now undertaken the effect of sodium lauryl sulphate micelles on the oxidation of *dl*-mandelic acid by Cr(VI) in aqueous medium.

Ip and Rocek have reported the oxidation of mandelic acid by Cr(VI) in which both C-H and C-C cleavages⁹ attached to the same carbon atom take place in one step. The oxidation is reported to follow a mixed kinetics of first and second order depending on the experimental conditions and is rationalised in terms of a three electron transfer in a single step. Although the report in pure aqueous medium was available, we undertook the oxidation in aqueous medium in order to have data in the presence and absence of NaLS under identical conditions to enable us to investigate into the role of NaLS micelles on the oxidation reactions.

Materials and Methods

dl-Mandelic acid (E. Merck), chromic acid (E. Merck) and perchloric acid (E. Merck), all analytical grade, were used as received. The surfactant sodium lauryl sulphate (NaLS) was used after recrystallisation from ethanol. Preparation of reactant solutions and kinetics were carried out as per details given earlier⁷.

Critical micellar concentration of the micelle in the presence of mandelic acid was observed to be same as reported earlier⁴ from this laboratory.

Results and Discussion

Kinetic studies in the absence of the surfactant

The oxidation was always carried out under the conditions of $[\text{mandelic acid}] \gg [\text{Cr(VI)}]$. Disappearance of Cr(VI), followed by iodometry, is observed to be first order at constant $[\text{H}^+]$ as seen from the linearity of $\log [\text{titre}]_t$ against time plots. Unit dependence in $[\text{Cr(VI)}]$ was further established from the constancy of first order rate constants when the oxidation studies were carried out using varying $[\text{Cr(VI)}]$.

In order to examine the influence of added [salt] on the oxidation, rates were measured in the presence of varying $[\text{K}_2\text{SO}_4]$ (Table 1). From the rate data it is observed that the pseudo-first order constant does not change implying that the oxidation is not affected by change of ionic strength of the medium. Hence in subsequent experiments no effort was made to maintain the ionic strength.

Effect of [mandelic acid] on the oxidation rates

Table 1—Substrate dependence of Cr(VI) oxidation of mandelic acid in the absence of micelle

$\{10^4 [\text{Cr(VI)}] = 9.853 \text{ mol dm}^{-3}, [\text{H}^+] = 0.172 \text{ mol dm}^{-3},$
temp. = 40°C, Aqueous medium. $\}$

[Mandelic Acid] (mol dm ⁻³)	[MnSO ₄] (mol dm ⁻³)	[K ₂ SO ₄] (mol dm ⁻³)	10 ⁵ <i>k_ψ</i> (S ⁻¹)
0.005			12 (18)
0.01			23 (31)
0.03			80 (75)
0.05			119 (126)
0.05	0.0001		123
0.05	0.0003		129
0.05	0.0005		117
0.05	0.0008		122
0.05	0.002		106 (125)
0.05	0.005		131 (140)
0.05	0.008		140 (153)
0.05	0.01		132 (130)
0.05		0.001	113 ^a
0.05		0.005	112 ^b
0.05		0.01	112 ^c
0.05		0.015	116 ^d
0.05		0.02	122 ^e
0.05		0.025	108 ^f
0.05		0.030	114 ^g
0.05		0.035	109 ^h
0.07			144 (168)
0.10			177 (192)
0.13			186 (204)
0.15			206 (216)

Values in parentheses denote *k_ψ* values in the presence of 0.008 mol dm⁻³ of NaLS.

was studied in the presence of 0.005 to 0.15 mol dm⁻³ mandelic acid. The rate data are given in Table 1. The rate increases with increase in [mandelic acid] with a tendency to attain a limiting value at high [mandelic acid]. Plot of *k_{obs}* against [mandelic acid] yielded a curve of concave nature (facing down) and plot of *k_{obs}*⁻¹ against [mandelic acid]⁻¹ (Fig. 1) is linear with a positive intercept and positive slope. Such a plot is indicative of Michaelis-Menten behaviour. It will be interesting to recall the work of Ip and Rocek who on the other hand reported first order and second order dependence in mandelic acid at low and high [mandelic acid] respectively characterised by curvature of concave nature upwards in the plot of *k_ψ* versus [mandelic acid].

Oxidation rates at different $[\text{HClO}_4]$ measured in the concentration range 0.17-0.54 mol dm⁻³ are included in Table 2. To arrive at a correlation the rate data were plotted against $[\text{H}^+]$. It is observed that the plot is linear with a small positive intercept and positive slope suggesting that the oxidation involves an acid independent and acid dependent step. From the small positive intercept, it is evident that contribution from the acid independent step to the overall rate is much smaller compared to that from acid dependent step. Further the following equilibrium¹⁴, Eq. (1),



controls the active Cr(VI) species.

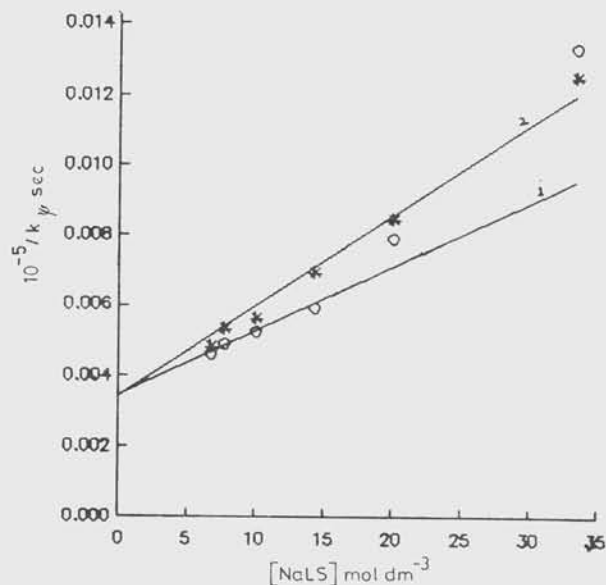


Fig. 1—Plot of $1/[\text{MA}]$ versus $10^{-5}/k_{\psi}$ $\{[\text{H}^+] = 0.172 \text{ mol dm}^{-3},$ temp. = 40°C; aq. medium; 1, $[\text{NaLS}] = 0.008 \text{ mol dm}^{-3}$; 2, absence of NaLS $\}$

Induced oxidation by Mn^{2+} has been extens-

Table 2—Acid dependence in the Cr(VI) oxidation of mandelic acid in the presence of sodium Lauryl sulphate at different temperatures

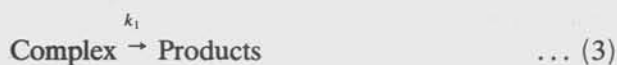
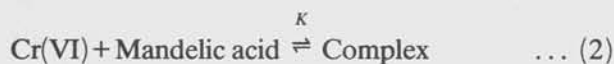
$\{10^4 [Cr(VI)] = 9.853 \text{ mol dm}^{-3}, [Mandelic \text{ acid}] = 0.05 \text{ mol dm}^{-3}, \text{aqueous medium.}\}$

[H ⁺] (mol dm ⁻³)	[NaLS] (mol dm ⁻³)	10 ⁵ k _p (s ⁻¹)			
		30°	35°	40°	45°C
0.09	0	—	—	68	—
	0.008	—	—	83	—
0.172	0	66	99	118	50
	0.005	68	105	125	155
	0.008	68	112	126	165
	0.01	74	103	136	177
	0.015	63	120	130	172
	0.025	77	108	108	132
	0.03	74	107	112	159
	0.05	72	100	119	130
	0.07	76	94	130	160
	0.10	76	96	151	177
0.27	0	—	—	169	—
	0.008	—	—	199	—
0.36	0	110	143	233	269
	0.005	122	142	240	283
	0.008	124	142	258	288
	0.01	129	154	260	299
	0.015	130	160	270	283
	0.025	117	120	262	224
	0.03	131	124	265	281
	0.05	103	139	237	256
	0.07	116	136	213	248
	0.10	110	135	231	239
0.54	0	128	203	295	332
	0.005	135	245	309	348
	0.008	145	251	311	366
	0.01	153	199	328	384
	0.015	155	192	242	342
	0.025	128	205	284	359
	0.03	135	253	313	332
	0.05	122	196	328	351
	0.07	134	204	291	349
	0.10	136	229	271	340
0.72	0	—	—	460	—
	0.008	—	—	528	—
0.90	0	—	—	569	—
	0.008	—	—	618	—
1.0	0	—	—	634	—
	0.008	—	—	679	—

ively used to trap Cr(IV) if formed in the rate limiting step. It is expected that oxidation rate by Cr(VI) would decrease by half in the presence of Mn(II) if Cr(IV) or Cr(V) is an intermediate¹³. With a view to find out intermediacy of Cr(IV) or Cr(V), oxidation rates, of mandelic acid by Cr(VI) were measured in the presence of varying [Mn(II)] and the rate data are collected in Table 1. It is observed from the data in Table 1 that the rate almost remains constant where [Mn²⁺] is varied in the range less than the [Cr⁶⁺] and the rate increases very nominally when Mn²⁺ is varied above [Cr(VI)]. In both ranges precipitation of MnO₂ was observed. When higher Mn²⁺ concentration was used, intermediacy of either Cr(IV) or Cr(V) is indicated. Intermediacy of Cr(V) in the rate limiting step is ruled out on the basis of negative polymerisation tests in the presence of radical forming reagents like acrylonitrile. It is thus evident that Cr(VI)-mandelic acid complex would decompose in the rate determining step involving two electron exchange in one step.

Enthalpy and entropy of activation have been computed from Eyring's equation¹⁵ and the data are given in Table 3. Enthalpy and entropy of activation values are not affected by change of [H⁺]. Negative entropy of activation although is characteristic of rate limiting formation of an intermediate complex^{16,17} or the chromic ester of mandelic acid, decomposition of the chromic ester of mandelic acid is still postulated as the rate limiting step due to the Michaelis-Menten kinetics observed. The negative entropy of activation then may arise from the difference in the entropy associated with the formation of the complex and large negative entropy associated with decomposition products due to solvation giving rise to a net negative entropy of activation. Such moderate negative entropy of activation has been observed in the oxidation of benzaldehyde¹⁸, 2-propanol¹⁹ and Ag(III) oxidation of hypophosphite²⁰ ion catalyzed by OH⁻ where in the decomposition of an intermediate complex has been postulated as the rate limiting step.

As Michaelis-Menten kinetics was observed, it is reasonable to assume that a complex between mandelic acid and Cr(VI) is formed which may break down in the slow step. Hence the oxidation steps may be written as



These steps would lead to the rate expression (4)

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{k_1 K [\text{MA}]_{\text{T}} [\text{Cr(VI)}]_{\text{T}}}{1 + K [\text{MA}]_{\text{T}}} \quad \dots (4)$$

or

$$k_{\text{obs}} = \frac{-d[\text{Cr(VI)}]/dt}{[\text{Cr(VI)}]_{\text{T}}} = \frac{k_1 K [\text{MA}]_{\text{T}}}{1 + K [\text{MA}]_{\text{T}}} \quad \dots (5)$$

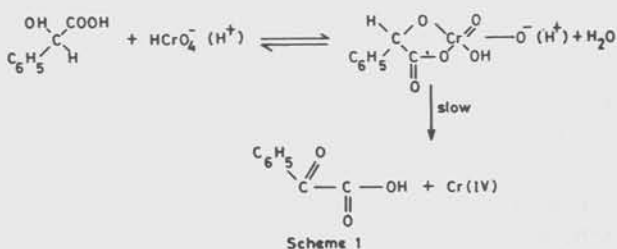
The expression suggests a linear relationship between k_{obs}^{-1} and $[\text{MA}]^{-1}$ which has been actually realised.

Further the acid variation shows an acid independent and acid dependent path and the overall rate expression comes out to be

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{(k' + k''[\text{H}^+]) K [\text{MA}]_{\text{T}} [\text{Cr(VI)}]_{\text{T}}}{1 + K [\text{MA}]_{\text{T}}} \quad \dots (6)$$

in which $k' \ll k''$

In the light of the rate law (Eq. 6) the oxidation pathway can be picturised as follows (Scheme 1).



Scheme 1 envisages formation of Cr(IV) in the slow step. Intermediacy of Cr(IV) has been confirmed from induced oxidation in the presence of Mn(II). Disproportion of Cr(IV) to Cr(III) then occurs in a fast step. However, the possibility of Cr(VI) being directly reduced to Cr(III) in a three electron process has been questioned recently¹⁰. The possible routes for disproportion of Cr(IV) is conversion of Cr(IV) to Cr(V) through the step



Cr(V) then reacts with a substrate molecule in a fast step giving the product i.e.



Further in the present study a direct three electron oxidation is not being envisaged in view of the Michaelis-Menten kinetics and no second or-

der dependence in mandelic acid has been observed. The product of oxidation is phenyl glyoxylic acid which is a product of two electron transfer.

Oxidation in the presence of sodium lauryl sulphate micelles

Pseudo-first order rate constants for the oxidation of mandelic acid by Cr(VI) in the presence of NaLS are incorporated in Table 1. The order each in $[\text{Cr(VI)}]$, $[\text{mandelic acid}]$ and $[\text{HClO}_4]$ is same as that observed in the absence of micelles. Further the rate is not affected by change of ionic strength as observed earlier. The activation parameters (Table 3) are also same as that observed in the absence of the micelle. These observations undoubtedly establish that the mechanism of oxidation of mandelic acid by Cr(VI) in the presence of NaLS remains same as in the absence of NaLS.

The effect of $[\text{NaLS}]$ on the pseudo-first order rate constant (k_{ψ}) at different acidities and temperatures are given in Table 2. Plots of k_{ψ} values against $[\text{NaLS}]$ shows (Fig. 2) marginal acceleration of rate till around CMC of NaLS but then decreases. The observation may be attributed to increasing solubilisation of the reactant species with increase in $[\text{surfactant}]$ which reaches a limiting value at CMC. Hence a rate maximum is obtained at CMC. Further increase in $[\text{surfactant}]$ results in increase in $[\text{micellar phase}]$ thus exerting a dilution effect on the reactant species resulting in gradual decrease of the rate. Observations of this type have been reported by Reinsborough and Robinson²¹ in metal complex formation reactions as well as by Bunton and Cerichelli²² in the oxidation of *n*-butylferrocene by ferric nitrate in the presence of NaLS.

The inhibition of the rate of oxidation of mandelic acid by Cr(VI) that occurs beyond the CMC

Table 3—Activation parameters for the oxidation of mandelic acid by Cr(VI) in presence of sodium lauryl sulphate at different temperatures.

$\{10^4 [\text{Cr(VI)}] = 9.853 \text{ mol dm}^{-3}, [\text{Mandelic acid}] = 0.05 \text{ mol dm}^{-3}, \text{aqueous medium}\}$			
$[\text{H}^+]$ (mol dm^{-3})	$[\text{NaLS}]$ (mol dm^{-3})	ΔH^\ddagger (kJ mol^{-1})	$-\Delta S^\ddagger$ ($\text{JK}^{-1} \text{mol}^{-1}$)
0.172	0	38.62	294.00
0.36	0	45.80	288.00
0.54	0	53.00	284.00
0.172	0.008	43.70	292.00
0.36	0.008	47.20	287.00
0.54	0.008	55.20	283.00

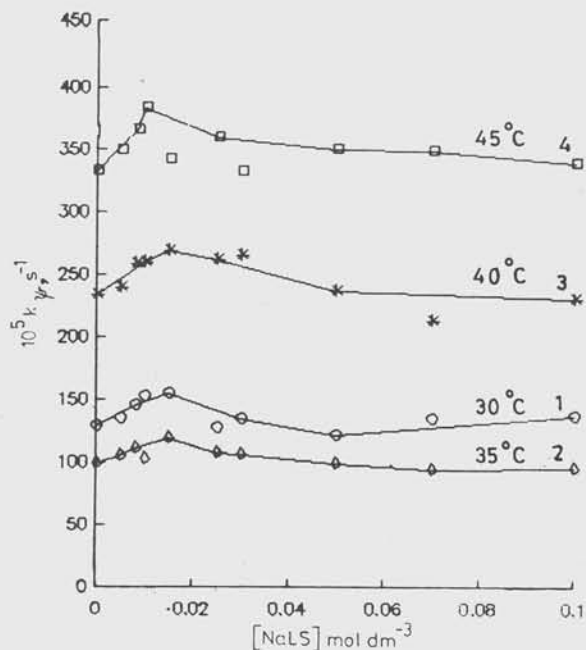


Fig. 2—Plot of $[\text{NaLS}]$ versus $10^5 k_\psi$ $[[\text{Mandelic acid}] = 0.05 \text{ mol dm}^{-3}; [\text{H}^+] = 1, 0.54; 2, 0.54; 3, 0.36; \text{ and } 4 = 0.54 \text{ mol dm}^{-3}]$

value is of interest and calls for explanation. Several models have been advanced to explain the inhibition of rates in the presence of micelle and important among them are those due to Menger and Portnoy²³ as well as of Berezin²⁴.

The Menger and Portnoy model which takes into consideration solubilisation of one reactant only into the micellar phase is given by Eq. 7.

$$k_\psi = \frac{k_w + k_M K_S ([D] - \text{CMC})}{1 + K_S ([D] - \text{CMC})} \quad \dots (7)$$

which can be modified to

$$\frac{1}{k_w - k_\psi} = \frac{1}{k_w - k_M} + \frac{1}{(k_w - k_M) K_S ([D] - \text{CMC})} \quad \dots (8)$$

When the kinetic data were fitted into Eq. (8) linearity in the plot of $(k_w - k_\psi)^{-1}$ versus $([D] - \text{CMC})^{-1}$ was not observed, implying that the model is inadequate for the present reaction. The plot of k_ψ against $[\text{NaLS}]$ showed a maximum around CMC of NaLS. Hence it is likely that both the reactions are partitioned between the bulk aqueous phase and the micellar pseudo-phase, since both hydrophobic and electrostatic interactions may be operative.

Therefore the reaction probably follows Scheme 2.

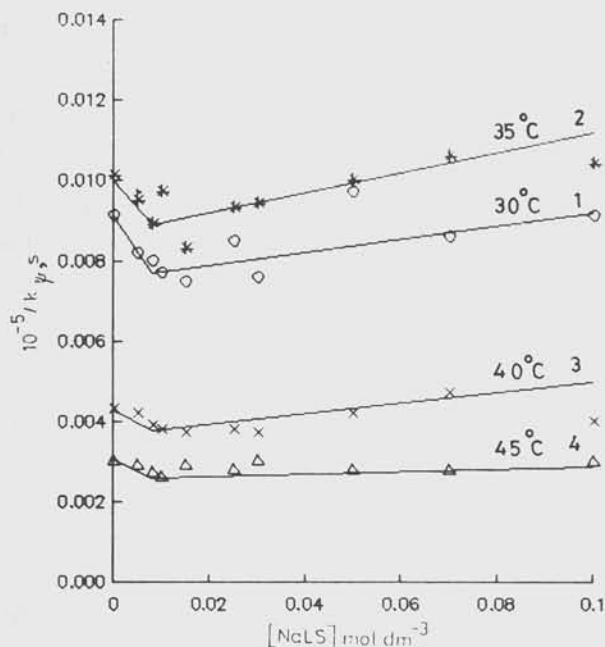
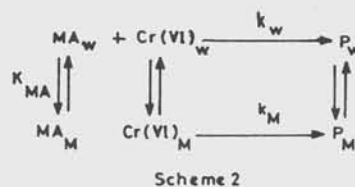


Fig. 3—Plots of $[\text{NaLS}]$ versus $10^{-5}/k_\psi$ $[[\text{Mandelic acid}] = 0.05 \text{ mol dm}^{-3}; [\text{H}^+] = 1, 0.36-2, 0.172; 3, 0.36; \text{ and } 4, 0.54 \text{ mol dm}^{-3}]$

It is possible to derive rate expression (9) from Scheme 2

$$k_\psi = \frac{k_w + \bar{k}_M K_{MA} K_{OX} C}{(1 + K_{MA} C)(1 + K_{OX} C)} \quad \dots (9)$$

Where k_w is the first order rate constant in absence of the micelle, K_{MA} and K_{OX} are the binding constants of mandelic acid and Cr(VI) with NaLS micelle respectively and C is the analytical concentration of NaLS. The rate in the aqueous medium can be neglected compared to the other term i.e. $\bar{k}_M K_{MA} K_{OX} C$ and rearranged to

$$\frac{1}{k_\psi} = \frac{1}{\bar{k}_M K_{MA} K_{OX} C} + \frac{K_{MA} + K_{OX}}{\bar{k}_M K_{MA} K_{OX}} + \frac{C}{\bar{k}_M} \quad \dots (10)$$

From Eq. 10 the trend of $1/k_\psi$ as a function of C would show a minimum at $C_{\min} = 1/(K_{MA} K_{OX})^{1/2}$ where as $1/k_\psi$ would be linearly dependent on C for $C > C_{\min}$. Figure 3 shows that a linear dependence exists between $1/k_\psi$ and C in the range from 8.0×10^{-3} to $9.0 \times 10^{-2} \text{ mol dm}^{-3}$. The value of \bar{k}_M obtained from the slope of the above plot at

different acidities and temperatures are given in Table 4. The rate data (\bar{k}_M) in pure micellar phase was fitted at Eyring equation to compute entropy of activation in pure micellar phase at different acidity. The entropy of activation computed using \bar{k}_M values are also given in Table 4. A comparison of ΔS^\ddagger values for aqueous medium and in presence of NaLS (Table 3) with that in pure micellar phase shows that entropy of activation in pure micellar phase is much less negative meaning that the intermediate complex is relatively labile to undergo easy fragmentation resulting in the products. Further the ratio of slope to intercept gives,

$K_{MA} K_{OX} / (K_{MA} + K_{OX})$ values. Making use of $C_{min} = \{K_{MA} K_{OX}\}^{-1/2}$ and slope to intercept ratio, K_{MA} and K_{OX} values at different acidities and temperatures have been computed and are summarized in Table 5. Numerous reactions with such rate maximum^{21,25} are known where it has been possible to compute the binding constants by the procedure described above. Examination of K_{MA} and K_{OX} values in Table 5 brings to light the following points.

(1) The binding constant K_{MA} decreases with increase of temperature whereas K_{OX} values increase with temperatures.

(2) There is increase of K_{MA} values with increase in acidity. On the contrary K_{OX} values decrease with acidity.

(3) The K_{MA} values are about few thousand fold higher than K_{OX} unlike in lactic acid oxidation where K_{LA} values were 40-50 fold higher than K_{OX} .

Transfer free energy^{26,27} per mole of the solute from water to the micellar phase can be calculated by the relationship.

$$\Delta\mu^0 = \mu_M^0 - \mu_w^0 = -RT \ln(55.5 K_B) \quad \dots (11)$$

where K_B is the binding constant of the respec-

Table 4—Rate constant in the pure micellar phase (\bar{k}_M) for the oxidation of mandelic acid by Cr(VI) in presence of sodium lauryl sulphate at different temperatures

$[10^4 \text{ [Cr(VI)]}] = 9.853 \text{ mol dm}^{-3}$, $[\text{Mandelic acid}] = 0.05 \text{ mol dm}^{-3}$, aqueous medium†

[H ⁺] (mol dm ⁻³)	$10^5 \bar{k}_M$ (dm ³ mol ⁻¹ s ⁻¹)				-ΔS [‡] (JK ⁻¹ mol ⁻¹)
	30°	35°	40°	45°C	
0.172	45	40	37	21	207
0.36	76	73	85	76	197
0.54	175	158	175	163	188

Table 5—Binding constants (K_{MA} and K_{OX}) in the micellar medium for the oxidation of Cr(VI) by mandelic acid in presence of sodium lauryl sulphate at different temperatures

$[10^4 \text{ [Cr(VI)]}] = 9.853 \text{ mol dm}^{-3}$, $[\text{Mandelic acid}] = 0.05 \text{ mol dm}^{-3}$, aqueous medium†

[H ⁺] (mol dm ⁻³)	K_{MA}				K_{OX}			
	30°	35°	40°	45°	30°	35°	40°	45°C
0.172	8843.54	5372.10	4104.00	1644.00	1.76	2.91	3.81	9.50
	(25268.30)	(15350.00)	(11727.00)	(4697.10)	(6.04)	(9.31)	(11.90)	(28.16)
0.36	9073.30	7156.00	4779.54	3752.10	1.72	2.20	3.27	4.20
	(25925.00)	(20446.00)	(13657.00)	(10721.24)	(5.92)	(7.24)	(10.34)	(12.90)
0.54	18593.00	11750.23	8070.00	6349.10	0.84	1.33	1.93	2.46
	(53124.00)	(33573.10)	(23058.00)	(18141.30)	(3.40)	(4.80)	(6.53)	(8.03)

Values in parenthesis are the partition coefficients (P_{MA} and P_{OX})

Table 6—Transfer of free energy from water to micelle in the oxidation of Cr(VI) by Mandelic acid at different temperatures

$[10^4 \text{ [Cr(VI)]}] = 9.853 \text{ mol dm}^{-3}$, $[\text{Mandelic acid}] = 0.05 \text{ mol dm}^{-3}$, aqueous medium†

[H ⁺] (mol dm ⁻³)	-Δμ ⁰ (k cal mol ⁻¹)							
	A				B			
	30°	35°	40°	45°	30°	35°	40°	45°C
0.172	7889.30	7714.43	7672.20	7216.57	2760.58	3111.40	3329.45	3960.76
0.36	7904.74	7889.87	7766.97	7738.11	2745.35	2935.93	3234.54	3439.25
0.54	8336.69	8193.41	8092.74	8070.48	2313.56	2632.63	2908.71	3106.98

tive reactants. $\Delta\mu^0$ values computed by the above equation for both mandelic acid and chromic acid have been given in Table 6.

It is interesting to note that $\Delta\mu^0$ values are much higher for mandelic acid than for the oxidant clearly indicating that the substrate species, mandelic acid, is involved in hydrophobic interaction with the micelle in its core^{28,29}. Consequently small $\Delta\mu^0$ values obtained for the oxidant species may be attributed to the orientation of the oxidant species on the outer surface^{26,27,30} of the micellar phase due to electrostatic or hydrophilic forces. Differential orientation of the reactant species within the micellar phase appear to be the cause of not too large acceleration.

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References

- 1 Tanford C, *The hydrophobic effect*, (1973) (Wiley, New York).
- 2 Sutin N, *Inorganic biochemistry*, edited by G I Eichhorn (Elsevier, Amsterdam), Vol 2 (1973) Ch. 19.
- 3 Piszkiwicz D, *J Am chem Soc*, 99 (1977) 7695.
- 4 Mishra S K & Panigrahi G P, *J chem Res (M)*, (1990) 1259.
- 5 Panigrahi G P & Mishra S K, *Indian J Chem*, 32A (1993) 956.
- 6 Panigrahi G P & Mishra S K, *Indian J Chem*, 31A (1992) 730.
- 7 Panigrahi G P & Mishra S K, *J mol Catal*, 81 (1993) 349.
- 8 Ip D & Rocek J, *J org Chem*, 44 (1979) 312.
- 9 Ip D & Rocek J, *J Am chem Soc*, 101 (1979) 6311, and reference therein.
- 10 Samal P C, Patnaik B B, Rao Dharma & Mahapatro S N, *Tetrahedron*, 14 (1981) 141.
- 11 Panigrahi G P & Sahu S K, Unpublished data.
- 12 Laidler K J, *Chemical kinetics*, (Tata McGraw Hill, Bombay) (1985) P. 440.
- 13 Bettie J K & Haight G P (Jr), *Inorganic reaction mechanism* (edited by J O Edwards) (Inter Science, New York), 132.
- 14 Westheimer F H, *Chem Rev*, 45 (1949) 419.
- 15 Espenson J H, *Chemical kinetics & reaction mechanism* (Mc-Graw Hill, New York) (1981) P. 157.
- 16 Willkins R G, *The study of kinetics and mechanism of reactions of transition metal complexes*, (Allyn and Bacon, Boston), (1974) P. 273.
- 17 Rizkalla E N, Lajuhen J L H & Choppin G R, *Inorg chim Acta*, 119 (1986) 93-98.
- 18 Lee D G & Spitzer U A, *Can J Chem*, 53 (1975) 3709.
- 19 Lee D G & Johnson D T, *Can J Chem*, 43 (1965) 1952.
- 20 Mehrotra R N & Kirschen Baum L J, *Inorg Chem*, 28 (1989) 4327.
- 21 Reinsborough V C & Robinson B H, *J chem Soc*, (Faraday 1), 75 (1979) 2395.
- 22 Bunton C A & Cerichelli G, *Int J chem Kinet*, 11 (1980) 539.
- 23 Menger F M & Portnoy C E, *J Am chem Soc*, 89 (1967) 4698.
- 24 Berezin I V, Martinek A K & Yatsimirskii, *Russ Chem Rev (Eng Trans)*, 42 (1973).
- 25 Carbone A I, Cayasino F P, Dio E D & Shrizilo C, *Int J chem Kinet*, 18 (1986) 609.
- 26 Bunton C A & Sepulveda L, *J phy Chem*, 83 (1979) 680.
- 27 Hirose C & Sepulveda L, *J phy Chem*, 85 (1981) 3689.
- 28 Tanford C, *The hydrophobic effect*, (Wiley, New York) (1973), Birdim K S, *Micellisation, solubilization and microemulsion*, Vol. 1 (edited by K L Mittal), (Plenum, New York), (1979) 151.
- 29 Wishnia A, *J phy Chem*, 67 (1963) 2079.
- 30 Pramauro E & Pellizzetti E, *Anal chim Acta*, 126 (1981) 253, *Ann Chim (Rome)*, 72 (1982) 117.