

Micellar effect: evidence in favour of different mechanistic paths of chromium(VI) oxidation of formic acid and oxalic acid in aqueous acid media[†]

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The cationic surfactant, cetylpyridinium chloride (CPC) inhibits the Cr^{VI} oxidation of formic acid in a monotonic fashion in aqueous H₂SO₄ media. On the other hand, under comparable conditions, CPC catalyses the Cr^{VI} oxidation of oxalic acid and then it inhibits the reaction after attaining a maximum value in the rate vs [CPC]_T profile. The observed micellar effect has been explained in the light of the proposed reaction mechanism and it provides an indirect evidence in favour of 3e⁻ transfer step for Cr^{VI} oxidation of oxalic acid.

Keywords: micellar effect, chromium(vi) oxidation, formic acid

Kinetic studies of Cr^{VI} oxidation of formic acid¹ and oxalic acid² have been carried out by different workers. In the case of oxalic acid, different workers have proposed different mechanistic routes. Oxalic acid can itself catalyse the Cr^{VI} oxidation of different substrates and in many cases it experiences cooxidation through three-electron transfer at a single step.³ To explain the second-order oxidation of oxalic acid by Cr^{VI}, Rocek *et al.*² suggested the three-electron transfer step. In fact, formic acid and oxalic acid behave differently in Cr^{VI} oxidation. This is why, it is worth exploring the effect of cetylpyridinium chloride (CPC, a representative cationic surfactant) on the title reactions under comparable conditions. Our preliminary observation indicated that CPC retards the oxidation of formic acid, but it catalyses the oxidation of oxalic acid. To avoid the solubility problem, effect of CPC was carried out only in aqueous H₂SO₄ media.

Under the experimental conditions, [S]_T >> [Cr^{VI}]_T in aqueous acidic media, both the substrates (*i.e.* HCO₂H, (CO₂H)₂ denoted by S) are oxidised to CO₂. The rate of disappearance of Cr^{VI} shows a first-order dependence on [Cr^{VI}]. Under the experimental conditions, [S]_T = 0.03–0.12 mol/dm³ (for (CO₂H)₂); 0.5–3.0 mol/dm³ (for HCO₂H), [H₂SO₄] = 1.0 mol/dm³, [Cr^{VI}] = 2 × 10⁻³ mol/dm³, the dependence on [S]_T is:

$$k_{\text{obs}} = k_5[S]^x \quad (1)$$

$x = 1$ for HCO₂H and $= 2$ for (CO₂H)₂. The values of $10^2 k_5/\text{dm}^6/\text{mol}^2/\text{s}$ at 35°C for (CO₂H)₂ are: 8.6 ± 0.1 (without CPC), and 22.8 ± 0.2 (at [CPC]_T = 2 × 10⁻³ mol/dm³). For HCO₂H, $10^4 k_5/\text{dm}^3/\text{mol}^2/\text{s}$ values (at 35°C) are: 3.15 ± 0.07 (without CPC) and 2.25 ± 0.05 (at [CPC]_T = 4 × 10⁻³ mol/dm³). It indicates that CPC catalyses the oxidation of (CO₂H)₂ while it inhibits the oxidation of HCO₂H. To investigate the effect of [H⁺] on k_{obs} , studies were carried out in aqueous HClO₄ media. For (CO₂H)₂, [S]_T = 0.05 mol dm⁻³, [Cr^{VI}] = 2 × 10⁻³ mol/dm³, I = 1.5 mol/dm³, $10^4 k_{\text{obs}}/\text{s}$ remains more or less constant in the range of [H⁺] = 0.35–1.0 mol dm⁻³ and at higher acidity it shows a slight decreasing trend. For HCO₂H, it shows a second-order dependence on [H⁺], *i.e.*

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

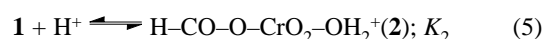
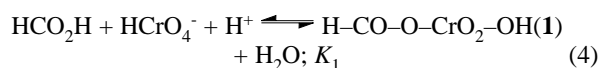
where, $k_{\text{H}} = (7.5 \pm 0.4) \times 10^{-4} \text{ dm}^6/\text{mol}^2/\text{s}$ at [HCO₂H]_T = 1.0 mol/dm³, [Cr^{VI}]_T = 2 × 10⁻³ mol/dm³, I = 1.5 mol/dm³, at 35°C.

The effect of [CPC]_T is shown in Fig. 1. For formic acid the rate continuously decreases and it attains a limiting value at higher [CPC]_T. The similar micellar effect has been noted in some cases.⁴ For (CO₂H)₂, the rate initially increases and attains a maximum value and then it decreases.

Thus the observed rate law under the said experimental conditions is:

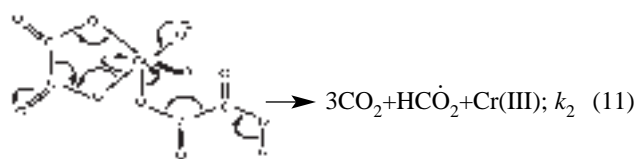
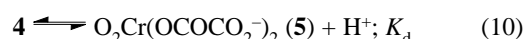
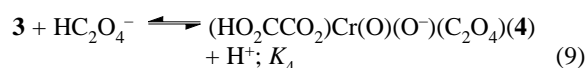
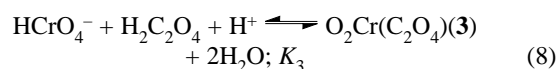
$$-\text{dln}[\text{Cr}^{\text{VI}}]/\text{dt} = k_{\text{obs}} = k[\text{S}]_T^x[\text{H}^+]^y \quad (3)$$

where $x = 2$, $y \approx 0$ for (CO₂H)₂ and $x = 1$, $y = 2$ for HCO₂H. The proposed mechanisms^{1,2} are:



Scheme 1

Cr^{VI} oxidation of formic acid



(4)

Scheme 2

Cr^{VI} oxidation of oxalic acid

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

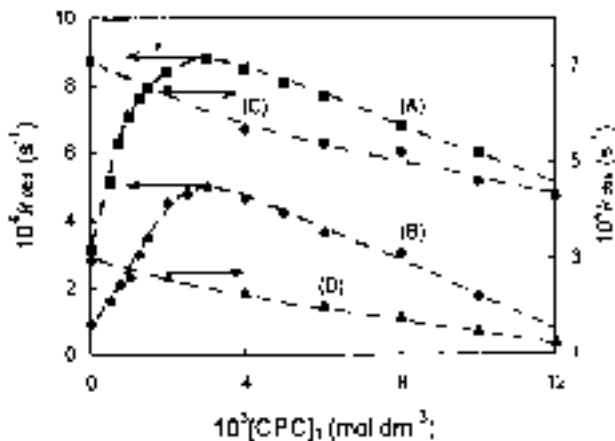


Fig. 1 Effect of $[\text{CPC}]_T$ on k_{obs} for the Cr^{VI} oxidation of oxalic acid (A, B; $[(\text{CO}_2\text{H})_2]_T = 0.06 \text{ mol/dm}^3$) and formic acid (C, D; $[\text{HCO}_2\text{H}]_T = 2.25 \text{ mol/dm}^3$) in aqueous H_2SO_4 media. $[\text{Cr}^{\text{VI}}]_T = 2.0 \times 10^{-3} \text{ mol/dm}^3$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol/dm}^3$. A (35°C); B (25°C); C (35°C); D (20°C).

Under the experimental conditions, concentration of H_2CrO_4 (*c.f.* $K_a \geq 10^5$) is negligibly small. Considering the quite low values of K_1 and K_2 , Scheme 1 leads to rate law (Eqn (12a)) which conforms to the experimental observation (*c.f.* Eqn (3)). Cr^{IV} formed can react in different possible ways⁶ in the subsequent faster reactions.

$$k_{\text{obs}} = K_1 K_2 k_1 [\text{S}]_T [\text{H}^+]^2 \quad (12a)$$

Scheme II leads to the following rate law (Eqn (12b)) for oxalic acid (assuming $[\text{S}] \approx [\text{S}]_T$, *c.f.* $K_a \approx 0.06$)²,

$$k_{\text{obs}} = k_2 K_3 K_4 K_a [\text{S}]_T^2 / \{1 + K_3 [\text{S}]_T [\text{H}^+] + K_3 K_4 K_d K_a [\text{S}]_T^2 / [\text{H}^+]\} \quad (12b)$$

By considering the magnitudes of K_3 , K_4 , K_d and K_a under the present experimental conditions. Eqn (12b) reduces to Eqn (13), which conforms to the experimental rate law.

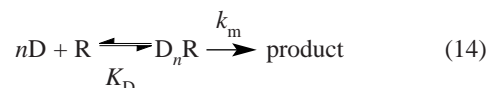
$$k_{\text{obs}} = k_2 K_3 K_4 K_a [\text{S}]_T^2 \quad (13)$$

The neutral complex (3) is proposed to have a cyclic structure, while the *bis*-complexes (4 and 5) are proposed to have the open-chain structures². The monoanionic complex (4) is only kinetically active towards the redox decomposition through 3e-transfer step (*c.f.* Eqn (11)), but the dianionic species (5) is not kinetically active. The 3e-transfer step directly leads to Cr^{III} avoiding the formation of unstable Cr^{IV} species. The produced $\text{CO}_2\text{H}^\bullet$ is relatively more stable and at the next faster steps it may react with Cr^{VI} or recombine or disproportionate. The intermediates Cr^{IV} and Cr^{V} are labile to form complexes with oxalic acid and it explains the formation of Cr^{III} -oxalic acid complexes along with $\text{Cr}(\text{H}_2\text{O})_6^{3+}$.

The continuous rate retardation by CPC in the case of formic acid can be explained by considering the fact that the neutral Cr^{VI} -ester (1) is preferably partitioned in the micellar interphase (probably in the Stern layer) but it needs protonation for redox decomposition (*c.f.* Eqn (6)). The cationic micellar head-groups repel the approach of H^+ and restrict the reaction to go on only in aqueous phase where concentration of 1 is significantly decreased. For oxalic acid, the neutral ester (3) is again preferentially accumulated in the micellar pseudo-phase and the cationic micellar phase is also enriched with the anionic oxalate species that combines with 3 to form the reactive species 4. It explains the micellar catalysis at relatively lower concentration of CPC. The rate inhibition occurs followed by

the maxima at relatively higher concentration of CPC. It is believed⁷ that once there is sufficient detergent to take up all the reactant species due to micellar solubilisation, addition of more surfactant merely exerts a dilution effect on the solubilised reactant species resulting a gradual decrease of the rate. Besides this, increased surfactant concentration increases the counterion (*i.e.* Cl^-) concentration and these counterions inhibit the approach of the reactive ionic reactant (*i.e.* HC_2O_4^-). In terms of Piszkiwicz model⁸ at higher $[\text{surfactant}]_T$, due to the further addition of surfactant molecules to the catalytically active reactant-surfactant aggregates makes them kinetically inactive.

The observed micellar effect can be analysed by considering the Piszkiwicz model⁸ where the neutral reactant (R) forms the catalytically active micelle, D_nR at lower concentration of the surfactant and it becomes kinetically inactive at higher concentration of the surfactant forming $\text{D}_n\text{D}_n\text{R}$.



Scheme 3

Piszkiwicz model for micellar catalysis and inhibition.

Scheme 3 leads to:

$$k_{\text{obs}} = (k_m [\text{D}]_T^n + k_w K_D) / \{K_D + [\text{D}]_T^n + K_{n'} [\text{D}]_T^n [\text{D}]_T^{n'}\} \quad (16)$$

Here k_w and k_m are the first-order rate constants in aqueous and micellar phase respectively. K_w is taken the corresponding rate constant in the absence of detergent while k_m is taken the maximum value of k_{obs} from the k_{obs} vs $[\text{CPC}]_T$, *i.e.* k_{obs} vs $[\text{D}]_T$ profile (for oxalic acid). At low detergent concentration, Eqn (16) reduces to Eqn (17) after rearrangement.

$$\log(P) = \log[(k_{\text{obs}} - k_w)/(k_m - k_{\text{obs}})] = n \log[\text{D}]_T - \log K_D \quad (17)$$

At high detergent concentration, Eqn (17) reduces to (18) after rearrangement.

$$\log(Q) = \log[(k_m/k_{\text{obs}}) - 1] = \log K_{n'} + n' \log[\text{D}]_T \quad (18)$$

In the case of formic acid, the micellar inhibition goes on monotonically and in such cases, Eqn 17 may be applied^{4b-d} to determine the kinetic parameters (taking $k_m = 0$). For oxalic acid, under the conditions, $[\text{S}]_T = 0.06 \text{ mol/dm}^3$, $[\text{Cr}^{\text{VI}}]_T = 2 \times 10^{-3} \text{ mol/dm}^3$, $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol/dm}^3$, at 25°C the values of kinetic parameters are: $n = 1.9$, $n' = 3.3$, $-\log K_D = 5.6$, $\log K_{n'} = 6.8$. For formic acid, under the conditions, $[\text{S}]_T = 2.25 \text{ mol/dm}^3$, $[\text{Cr}^{\text{VI}}]_T = 2 \times 10^{-3} \text{ mol/dm}^3$, $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol/dm}^3$, at 35°C the corresponding values are: $n = 1.3$, $-\log K_D = 2.5$. The orders of these kinetic parameters are quite reasonable⁸ in comparison with other micelle catalysed reactions subjected to this model. The values of n ($= 1-2$), far less than the aggregation number (20 to 100) of the surfactant molecules⁸ leading to the micelles indicate the existence of catalytically productive submicellar aggregates.

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