SHORT PAPER

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Cooxidation of formic acid and oxalic acid by chromium(VI) in aqueous acid media: a kinetic study[†]

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The Cr(VI) oxidation of a mixture of formic acid and oxalic acid in aqueous acid media occurs much faster than that of either of the two substrates alone; in the mixture, both substrates undergo oxidation simultaneously in a ternary complex of Cr(VI) through a three-electron transfer step (*i.e.* Cr(VI) → Cr(III)).

Keywords: formic acid, oxalic acid, chromium(VI)

Kinetics of oxidation of formic acid[1] and oxalic acid[2] by chromic acid have been studied by different workers. Their mechanism of oxidation is different. For oxalic acid, the rate determining step involves a 3*e*-transfer in the redox decomposition of the *bis*-complex of Cr(VI) while for formic acid, the rate determining step involves a 2*e*-transfer in the redox decomposition of the *mono*-complex of Cr(VI). Their rate law is given by :

$$k_{obs} = -\,d\ln[Cr(IV)]/dt = k[S]_T^x\,[H^+]^y \qquad (1)$$

where $x = 2$, $y \approx 0$ for S = $H_2C_2O_4$ and $x = 1$, $y = 2$ for S = HCO_2H. Under experimental conditions, the rate of oxidation of formic acid is very slow while that of oxalic acid is moderately fast. Our preliminary observations indicate that the rate of Cr(VI) oxidation of their reaction mixture is dramatically accelerated. In fact, oxalic acid is known[3] to catalyse the Cr(VI) oxidation of different types of substrates. To explore the detailed mechanism of the catalysed cooxidation of formic acid and oxalic acid, the present investigation has been undertaken. It appears also worth exploring from the standpoint of comparison with the mechanism of oxidation of the substrates alone.[1,2]

Under the experimental conditions, $[HCO_2H]_T$, $[H_2C_2O_4]_T$ >> $Cr(VI)]_T$ in aqueous acid media, the substrates are simultaneously oxidised to CO_2. The rate of disappearance of [Cr(IV)] shows a first-order dependence on [Cr(VI)]. In the presence of both substrates, Cr(VI) is likely to be consumed in three possible ways, *i.e.* independent oxidation of formic acid (*i.e.* $k_{obs(f)}$) and oxalic acid (*i.e.* $k_{obs(o)}$); and catalysed cooxidation of the substrates (*i.e.* $k_{obs(cat)}$). Thus the observed rate constant ($k_{obs(T)}$) for the reaction mixture is given by:

$$k_{obs(T)} = k_{obs(f)} + k_{obs(o)} + k_{obs(cat)} \qquad (2)$$

From the variation of $[HCO_2H]_T$ in the range, 0.04–0.2 mol/dm^3 at fixed $[Cr(IV)]_T$ and $[H_2C_2O_4]_T$ in 1.0 mol/dm^3 H_2SO_4, the plot of $k_{obs(T)}$ *vs* $[HCO_2H]_T$ gives a linear plot (Fig. 1) with a finite intercept (*a*) measuring the contribution of oxidation of oxalic acid alone under the experimental conditions. This has been confirmed from an independent experiment of Cr(VI) oxidation of oxalic acid in the absence of formic acid. Thus from the experimental fit, the rate equation is:

$$k_{obs(T)} = a + b[HCO_2H]_T \qquad (3)$$

The slope (*b*) measures the contribution of both independent oxidation of HCO_2H and oxalic acid catalysed oxidation of HCO_2H. From the effect of $[H_2C_2O_4]_T$ on $k_{obs(T)}$ (Fig. 2), it is evident that no oxalic acid independent path measuring the contribution from the uncatalysed oxidation of formic acid is noticed. It is also supported from an independent experiment that under the conditions used, the rate of oxidation of formic acid alone is negligibly small. The plot of $k_{obs(T)}/[H_2C_2O_4]_T$ *vs* $[H_2C_2O_4]_T$ is linear (Fig. 2) with a positive intercept. From the experimental fit, the observed relationship is:

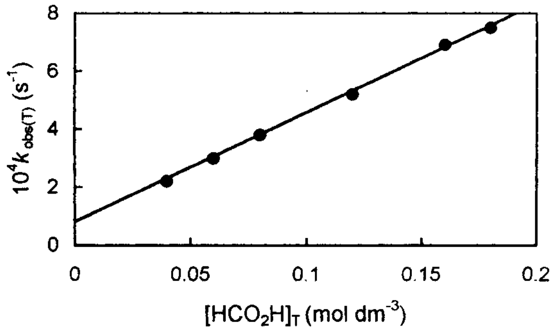

Fig. 1 Effect of $[HCO_2H]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of the reaction mixture containing both HCO_2H and $H_2C_2O_4$ in aqueous H_2SO_4 media. $[Cr(VI)]_T$ = 2x10^{-3} mol dm^3, $[H_2C_2O_4]_T$ = 0.03 mol/dm^3; $[H_2SO_4]$ = 1.0 mol/dm^3, 35 °C.

$$k_{obs(T)} = c[H_2C_2O_4]_T + d[H_2C_2O_4]_T^2 \qquad (4a)$$
$$i.e.\ \ k_{obs(T)}/[H_2C_2O_4]_T = c + d[H_2C_2O_4]_T \qquad (4b)$$

The *d*-path (*i.e.* second-order oxidation of oxalic acid) originates from the oxidation of oxalic acid alone and the *c*-path arises from the catalysed cooxidation path. From the H$^+$-variation experiment, under the conditions $[Cr(IV)]_T$ = 2×10^{-3} mol/dm^3, $[H_2C_2O_4]$ = 0.03 mol/dm^3, $[HCO_2H]_T$ = 0.04 mol/dm^3, [H$^+$] = 0.35–1.2 mol/dm^3, *I* = 1.5 mol/dm^3, at

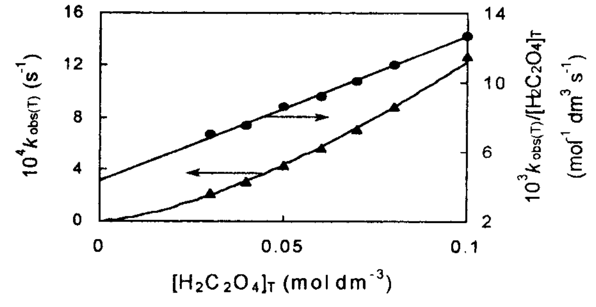

Fig. 2 Effect of $[H_2C_2O_4]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of the reaction mixture containing both HCO_2H and $H_2C_2O_4$ in aqueous H_2SO_4 media. $[Cr(VI)]_T$ = 2x10^{-3} mol/dm^3, $[HCO_2H]_T$ = 0.04 mol/dm^3, $[H_2SO_4]$ = 1.0 mol/dm^3, 35 °C.

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

35 °C, it is found that $k_{obs(T)}$ is constant (*ca* 6.5×10^{-4}/s, 35 °C) and thus it is independent of $[H^+]$. From an independent experiment, the rate of oxidation of oxalic acid alone under the experimental conditions is found independent of $[H^+]$ and this path (*i.e.* $k_{obs(ox)}$) contributes *ca* 3.5×10^{-4}/s. Under the experimental conditions, the rate of oxidation of formic acid alone is very slow and this path (*i.e.* $k_{obs(f)}$) contributes *ca* 0.35×10^{-4} s^{-1} at $[H^+] = 1.2$ mol/dm^3 (maximum value used in the experiment). Thus under the experimental conditions, $k_{obs(T)}$ arises only from the contribution of $k_{obs(o)}$ and $k_{obs(cat)}$. Under the different experimental conditions, where the rate is quite measurable, the rate of oxidation of formic acid alone shows a second order dependence on $[H^+]$. Thus the complete rate law is:

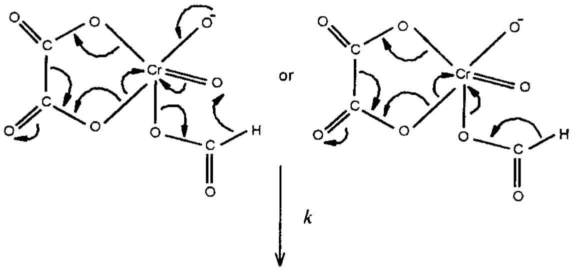
$$k_{obs(T)} = k_f[HCO_2H]_T[H^+]^2 + k_o[H_2C_2O_4]^2 + k_{cat}[HCO_2H]_T[H_2C_2O_4]_T \tag{5}$$

Comparing eqns (3)–(5), the following relations are obtained. $a = k_o[H_2C_2O_4]_T{}^2$, $b = k_f[H^+]^2 + k_{cat}[H_2C_2O_4]_T$ and $c = k_{cat}[HCO_2H]_T$, and $d = k_o$. The estimated value of 10^2k_o/dm^6/mol^2/s (= 8.9 ± 0.1) nicely conforms to the reported value[2b] (= 8.6 ± 0.1) in 1.0 mol/dm^3 H_2SO_4 at 35 °C. By using the reported value[2b] of $k_f[H^+]^2$ (= 3.15×10^{-4} dm^3/mol/s in 1.0 mol/dm^3 H_2SO_4 at 35 °C), the k_{cat} value is found $(11.45 \pm 0.10) \times 10^{-2}$ dm^6/mol^2/s by using the relation, $b = k_f[H^+]^2 + k_{cat}[H_2C_2O_4]_T$ (*c.f.* the plot of $k_{obs(T)}$ *vs* $[HCO_2H]_T$, Fig. 1). From the $[H_2C_2O_4]_T$ variation experiment (Fig. 2) (where the contribution of $k_f[HCO_2H]_T[H^+]^2$ is negligibly small), the plot of $k_{obs(T)}/[H_2C_2O_4]_T$ *vs* $[H_2C_2O_4]_T$ leads to : $k_o = 8.4 \times 10^{-2}$ dm^6/mol^2/s and $k_{cat} = 10.80 \times 10^{-2}$ dm^6/mol^2/s at 35 °C in 1.0 mol/dm^3 H_2SO_4. These values are in good agreement with those obtained from the $[HCO_2H]_T$ variation experiment.

The Cr(VI) oxidation of formic acid[1] involves the formation of Cr(VI)–formic acid ester which experiences an acid catalysed redox decomposition through a 2*e*-transfer step. The oxidation of oxalic acid[2] passes through the formation of a *bis*-complex of Cr(VI) followed by the redox decomposition of the complex through a 3*e*-transfer step. The catalysed cooxidation of formic acid and oxalic acid can be explained by considering the Rocek mechanism[3] which considers the formation of a ternary complex of Cr(VI) involving both $H_2C_2O_4$ and HCO_2H and the decomposition of the mixed ligand complex through a 3*e*-transfer step at the rate-determining step. Ignoring the dissociation of $H_2C_2O_4$ (pK_1 = 1.27)[4] and HCO_2H (pK = 3.75)[4] the following reaction steps can explain all the observations:

$$HCrO_4^- + H_2C_2O_4 + H^+ \rightleftharpoons O_2Cr(C_2O_4)\ (\mathbf{1}) + 2H_2O,\ K_1 \tag{6}$$

$$\mathbf{1} + HCO_2H \rightleftharpoons (C_2O_4)Cr(O)(O^-)(O_2CH)\ (\mathbf{2}) + H^+,\ K_2 \tag{7}$$



(8)

$$CO_2^{\bullet -} + Cr(VI) \longrightarrow Cr(V) + CO_2,\ \text{fast} \tag{9}$$

$$Cr(V) + H_2C_2O_4 \longrightarrow 2CO_2 + Cr(III) + 2H^+,\ \text{fast} \tag{10}$$

$$Cr(V) + HCO_2H \longrightarrow CO_2 + Cr(III) + 2H^+,\ \text{fast} \tag{11}$$

Scheme 1 Cooxidation of formic acid and oxalic acid by Cr(VI).

The ternary complex (**2**) experiences the redox decomposition in a 3*e*-transfer step through a cyclic transition state giving rise to Cr(III) and $CO_2^{\bullet -}$ (*c.f.* eqn (8)). Free radical generation is proved from the observation of acrylonitrile polymerisation. This 3*e*-transfer step avoids the formation of unstable Cr(IV) species. A similar reaction step occurs in the oxidation of oxalic acid alone. Scheme 1 leads to the following rate law measuring the contribution of the catalysed path.

$$k_{obs(cat)} = \frac{kK_1K_2[H_2C_2O_4][HCO_2H]_T}{1 + K_1[H^+][H_2C_2O_4]_T + K_1K_2[H_2C_2O_4]_T[HCO_2H]_T} \tag{12}$$

K_1 (≈ 5.0 mol^2/dm^6)[5] and K_2 are small under the experimental conditions and it is reasonable to assume, $1 \gg K_1[H^+][H_2C_2O_4]_T + K_1K_2[H_2C_2O_4]_T[HCO_2H]_T$. Thus eqn (12) reduces to:

$$k_{obs(cat)} = kK_1K_2[H_2C_2O_4]_T[\ HCO_2H]_T = k_{cat}[H_2C_2O_4]_T[HCO_2H]_T \tag{13}$$

Stoichiometry determination indicates that both formic acid and oxalic acid are simultaneously consumed, but the relative amount of each substrate consumed depends upon their relative concentrations. The reactions given by eqns (10) and (11) mutually compete and their relative importance depends on their relative concentration and reactivity. In addition to this, the uncatalysed paths also go on slowly simultaneously. Thus a fixed stoichiometry is not observed.

Experimental

Oxalic acid (AR, E. Merck), formic acid (AR, E. Merck), $K_2Cr_2O_7$ (AR, E. Merck), $HClO_4$ (AR, E. Merck) and H_2SO_4 (AR, E. Merck) were used without purification. All other chemicals used were of reagent grade. The rate of disappearance of Cr(VI) was followed by the titrimetric quenching technique estimating the concentration of Cr(VI) iodometrically.[6] The amount of oxalic acid reacted was estimated by $KMnO_4$ in acidic media without any accountable interference from formic acid and the amount of formic acid reacted was estimated[7] by alkaline $KMnO_4$ solution after the estimation of oxalic acid by acidic $KMnO_4$ solution and separation of Mn(II) as $Mn(OH)_2$.

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