Kinetics and Mechanism of Ruthenium(III) catalysed Oxidation of Formic Acid by Cerium(IV) in Aqueous Sulfuric Acid Media

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The kinetics of oxidation of formic acid by cerium(IV) in the presence of ruthenium(III) (*ca.* 10^{-6} mol dm^{-3}) in aqueous sulfuric acid media has been followed at different temperatures (30–50 °C). The rate of disappearance of cerium(IV) in the reaction has been found to be zero order with respect to cerium(IV) concentration. At a fixed $[H^+]$, under the conditions, $[HCO_2H]_T \gg [Ce^{IV}]_T \gg [Ru]_T$ the observed zero-order rate constant (k_0) conforms to: $-d[Ce^{IV}]_t/dt = k_0 = [Ru]_T[HCO_2H]_T\{k_b + k_c[HCO_2H]_T\}$ where $[Ru]_T$ and $[HCO_2H]_T$ represent the total concentration of ruthenium(III) and formic acid respectively. At 40 °C, $[H_2SO_4] = 1.0$ mol dm^{-3} and $I = 2.75$ mol dm^{-3} the values of 10^2k_b and 10^2k_c are 6.0 ± 0.1 dm^3 mol^{-1} s^{-1} and 5.4 ± 0.1 dm^6 mol^{-2} s^{-1} respectively. Both k_b and k_c are found to have an inverse hydrogen-ion dependence. Out of the different possible mono- and bis-complexes, $Ru^{III}(HCO_2^-)$ and $Ru^{III}(HCO_2^-)(HCO_2H)$ have been found to be kinetically active in the slow oxidative steps (through an inner-sphere mechanism) leading to $Ru^{III}H$ (through hydride transfer from the C–H bond of metal-bound formate) and CO_2 followed by the rapid oxidation of $Ru^{III}H$ to Ru^{III} by cerium(IV). The activation parameters are $\Delta H^\ddagger = 46 \pm 3$ kJ mol^{-1}, $\Delta S^\ddagger = -125 \pm 5$ J K^{-1} mol^{-1} (for the k_b path) and $\Delta H^\ddagger = 47 \pm 3$ kJ mol^{-1}, $\Delta S^\ddagger = -120 \pm 5$ J K^{-1} mol^{-1} (for the k_c path).

Oxidation of different types of organic compounds by cerium(IV) is well documented[1,2] and the kinetics of such reactions have been studied extensively.[3–17] Different catalysts like silver(I),[18,19] manganese(II),[12,20,21] copper(II),[19,22] osmium(VIII),[23] mercury(II),[24] chromium(III),[25] ruthenium(III),[26] iridium(III),[21,26d] bromide[27] iodine,[28] *etc.* have been used in oxidation reactions of cerium(IV). Among these different types of catalyst, ruthenium(III) and iridium(III) have been found to be highly efficient. In the case of ruthenium(III), different catalytic cycles such as Ru^{III}–Ru^{I}[26b,f] and Ru^{III}–Ru^{IV}[26c,d] have been reported in different systems.

Several metal ions[1,2,29] and metal complexes[30] have been utilised in following the oxidation of formic acid. In aqueous sulfuric acid, oxidation of formic acid by cerium(IV) in the absence of a catalyst is very sluggish.[2,17,25b,27,31] Our preliminary observations indicate that addition of traces of ruthenium(III) enhances the rate significantly and the catalysed reaction responds negatively to a test for free radicals in contrast to the uncatalysed reaction. This efficient catalysis and change of mechanism from free-radical to ionic prompted us to investigate thoroughly the kinetics and mechanism of ruthenium(III) catalysed oxidation of formic acid by cerium(IV) in aqueous sulfuric acid media.

Experimental

Materials and Reagents.—The cerium(IV) stock solution was obtained by dissolving $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ (A.R., E. Merck) in 1.0 mol dm^{-3} sulfuric acid and standardised with ammonium iron(II) sulfate solution using ferroin as indicator. Formic acid (A.R., E. Merck) solutions were prepared by dilution and standardised by alkaline permanganate[32] before use. Doubly crystallised $NaClO_4$ (L.R., Loba) was used to maintain ionic strength and was standardised by ion exchange through Dowex 50W-X8 cation exchanger in H^+ form.

Commercial ruthenium trichloride hydrate (Johnson Matthey) was purified[33a] by repeated evaporation with concentrated hydrochloric acid. To remove the last traces of ruthenium(IV), it was taken in the minimum volume of dilute hydrochloric acid (≈0.3 mol dm^{-3}) and treated with mercury.[33b] The solution was then taken up in warm 1.0 mol dm^{-3} sulfuric acid and allowed to stand for several days to attain equilibrium. This stock solution (*ca.* 1×10^{-3} mol dm^{-3}) in 1.0 mol dm^{-3} sulfuric acid responded negatively to a starch–iodide test[34] indicating the absence of ruthenium(IV). The solution ($\lambda_{max} = 295$ nm, $\varepsilon = 7.5 \times 10^2$ dm^3 mol^{-1} cm^{-1}) remained unchanged over a long period when kept in a glass-stoppered flask in a refrigerator. The concentration of ruthenium(III) in the stock solution was standardised as reported earlier.[35] All other chemicals used were of reagent grade. Doubly distilled water was employed throughout the experiments. The experimental conditions are given in detail in the Figures and Table 1.

Procedure and Kinetic Measurements.—The reaction was initiated by mixing the pre-equilibrated reactant solutions at the desired conditions and the progress of the reaction was monitored by withdrawing known amounts of aliquots of the reaction mixture at regular time intervals, quenching the reaction by adding a standard ammonium iron(II) sulfate solution in 2.0 mol dm^{-3} sulfuric acid in excess and back titrating the unreacted iron(II) ions against standard cerium(IV) solution using ferroin as indicator. A few kinetic runs were made spectrophotometrically (Beckman DU 6) at 320 nm where the other reagents and reaction products are almost non-absorbing under the experimental conditions. In this method, the aliquots of the reaction solution were diluted (40–50 fold) by addition of cold 1 mol dm^{-3} sulfuric acid to bring the cerium(IV) concentration to *ca* 10^{-4} mol dm^{-3}. This had the effect of markedly slowing down the reaction rate [*cf.* equation (3)] and no significant cerium(IV) consumption took place in the time interval between dilution and absorbance measurement. The oxidant concentration was evaluated from the absorbance ($\varepsilon = 5550$ dm^3 mol^{-1} cm^{-1}). The results were almost identical with those obtained by the titration method.

Here, it is worth mentioning that cerium(IV) in sulfuric acid–sulfate media is more stable than cerium(IV) in perchloric acid–perchlorate media (*cf.* $E_0 = 1.7$ V in 1 mol dm^{-3} $HClO_4$,

E_0 = 1.4 V in 1 mol dm^{-3} H_2SO_4). Cerium(IV) undergoes photochemical decomposition[36] very slowly leading to oxidation of water in perchloric acid–perchlorate media, but under the experimental conditions of the present investigation, cerium(IV) solutions are sufficiently stable.[7,37] Hence no precaution to exclude diffused light entering the reaction solution was taken.

Kinetic runs were performed in the presence of a large excess of substrate and sulfuric acid over the oxidant. Ionic strength was maintained by $NaClO_4$ and H_2SO_4 (taking the protonation constants[38] of SO_4^{2-} into consideration). Under the experimental conditions, the zero-order rate constants (k_0 = –slope[oxidant]$_t$ *vs.* time) were calculated from the linear plots (Fig. 1). Average values of at least two independent determinations of k_0 were taken. A few runs were also taken after bubbling purified dinitrogen or carbon dioxide and compared with those taken under air and the results were found to be the same.

Stoichiometry and Product Analysis.—Under the kinetic conditions, in the presence of the catalyst, excess formic acid was allowed to react with cerium(IV) in 1 mol dm^{-3} sulfuric acid (a representative set: $[Ce^{IV}]$ = 0.04 mol dm^{-3}, $[HCO_2H]$ = 0.06 mol dm^{-3}, $[Ru^{III}] = 4 \times 10^{-6}$ mol dm^{-3}) and after completion of the reaction indicated by the disappearance of the cerium(IV) colour, unreacted formic acid was estimated[32] after separation of cerium(III) as its hydroxide. From observations of different sets, the stoichiometry conforms to $2Ce^{IV} + HCO_2H \longrightarrow 2Ce^{III} + CO_2 + 2H^+$. This observation is in agreement with the generally accepted view[27,29] that formic acid is oxidised by metal ions or metal complexes into carbon dioxide. Under the kinetic conditions, carbon dioxide was qualitatively detected by purging dinitrogen through the reaction solution and passing the outcoming gas through a narrow tube containing $Ca(OH)_2$. Cerium(III) was detected qualitatively after separation as hydroxides from the reaction solution followed by treatment of $NaBiO_3$ in dilute HNO_3.

Results and Discussion

Dependence on Cerium(IV) *Concentration*.—In the presence of a large excess of formic acid over the oxidant, plots of [oxidant]$_t$ *vs.* time (t) were linear for more than 80% completion of reaction (see Fig. 1) indicating zero-order kinetics with respect to oxidant, equation (1) (at fixed $[H_2SO_4]$, catalyst concentration *i.e.* $[Ru]_T$ and $[HCO_2H]_T$).

$$-\frac{d[Ce^{IV}]_t}{dt} = k_0 \qquad (1)$$

Dependence on Ruthenium(III) *Concentration*.—In the presence of ruthenium(III) (*ca.* 10^{-6} mol dm^{-3}), k_0 shows a first-order dependence on the catalyst concentration (see Fig. 2) *i.e.* $[Ru]_T$, and the uncatalysed path remains kinetically non-existent [equation (2)] (at constant $[H_2SO_4]$, $[HCO_2H]_T$ and $[Ce^{IV}]_T$).

$$k_0 = k_a[Ru]_T \qquad (2)$$

The latter is also confirmed (see Fig. 1) by carrying out a blank run under the same kinetic conditions in the absence of catalyst.

Dependence on Formic Acid Concentration.—Plots of $k_0/[HCO_2H]_T$ *vs.* $[HCO_2H]_T$ are linear with positive intercepts (see Fig. 3) indicating two parallel paths involving first- and second-order dependence with respect to $[HCO_2H]_T$. This observation can be formulated by equation (3) (at fixed $[H_2SO_4]$, $[Ru]_T$ and $[Ce^{IV}]_T$). The values of k_b and k_c are given in Table 1.

$$\frac{k_0}{[Ru]_T[HCO_2H]_T} = k_b + k_c[HCO_2H]_T \qquad (3)$$

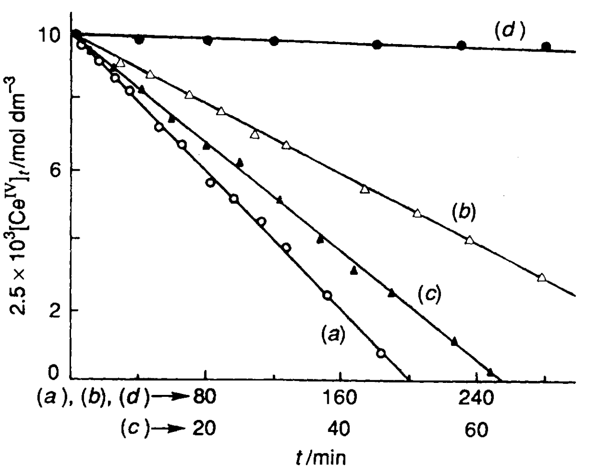

Fig. 1 Graphical evaluation of zero-order rate constants (k_0) for the oxidation of formic acid by cerium(IV) in the presence of ruthenium(III); $[Ce^{IV}] = 4 \times 10^{-3}$ mol dm^{-3}, $[Ru^{III}] = 3 \times 10^{-6}$ mol dm^{-3}, $[H_2SO_4]$ = 1.0 mol dm^{-3}, I = 2.75 mol dm^{-3}, 30 °C, $[HCO_2H]$ = 1.5 (*a*), 1.0 (*b*), 3.0 (*c*) or 1.5 mol dm^{-3} in absence of catalyst (*d*)

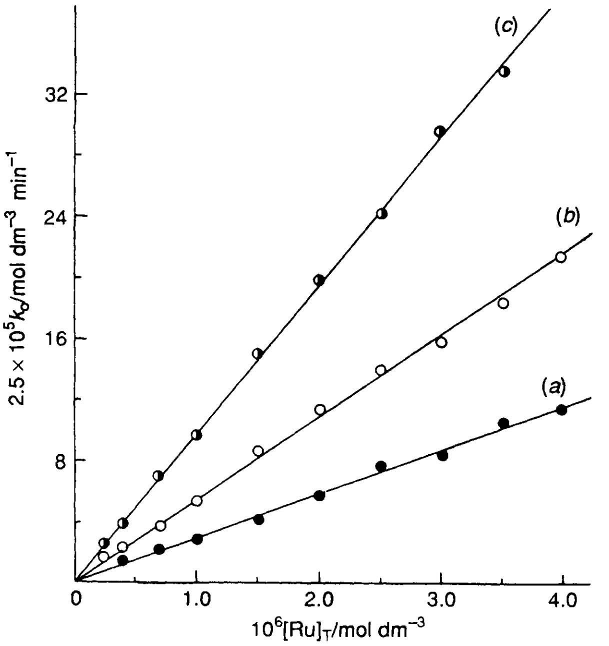

Fig. 2 Effect of ruthenium(III) on k_0 for the oxidation of formic acid by cerium(IV); $[Ce^{IV}] = 4 \times 10^{-3}$ mol dm^{-3}, $[HCO_2H]$ = 2.0 mol dm^{-3}, $[H_2SO_4]$ = 1.0 mol dm^{-3}, I = 2.75 mol dm^{-3}; T = 30 (*a*), 40 (*b*) or 50 °C (*c*)

Hydrogen Ion Dependence.—Plots of k_0 *vs.* $[H^+]^{-1}$ are linear (see Fig. 4) passing through the origin indicating the rate equation (4) (at fixed $[HCO_2H]_T$, $[Ru]_T$ and $[NaHSO_4]$).

$$k_0/[Ru]_T = y/[H^+] \qquad (4)$$

Variation of concentration of the hydrogen ion was carried out by varying $[HClO_4]$ at fixed $[NaHSO_4]$. At 40 °C, $y = 10.0 \times 10^{-2}$ mol dm^{-3} s^{-1} (at $[HCO_2H]_T$ = $[NaHSO_4]$ = 1.0 mol dm^{-3}).

Temperature Dependence.—Table 1 also collects the values of k_a, k_b and k_c at different temperatures and activation parameters (determined by Eyring plots[39]) for each path.

Table 1 Ruthenium(III) catalysed oxidation of formic acid by cerium(IV) in aqueous sulfuric acid media; $[Ce^{IV}]_T = 4 \times 10^{-3}$ mol dm^{-3}; $[Ru]_T = (0.25\text{–}4.0) \times 10^{-6}$ mol dm^{-3}; $[HCO_2H]_T = 0.25\text{–}4.0$ mol dm^{-3}; $[H_2SO_4] = 1.0$ mol dm^{-3}; $I = 2.75$ mol dm^{-3}

	$10k_a$/s^{-1}			
T/°C	Obs.	Calc.*	10^2k_b/dm^3 mol^{-1} s^{-1}	10^2k_c/dm^6 mol^{-2} s^{-1}
30	1.9 ± 0.1	1.9	3.1 ± 0.1	3.1 ± 0.1
40	3.6 ± 0.1	3.4	6.0 ± 0.1	5.4 ± 0.1
50	6.5 ± 0.1	6.2	9.7 ± 0.1	10.5 ± 0.2
$\Delta H^‡$/kJ mol^{-1}	47 ± 3		46 ± 3	47 ± 3
$\Delta S^‡$/J K^{-1} mol^{-1}	−106 ± 5		−125 ± 5	−120 ± 5

* By using the observed values of k_b and k_c.

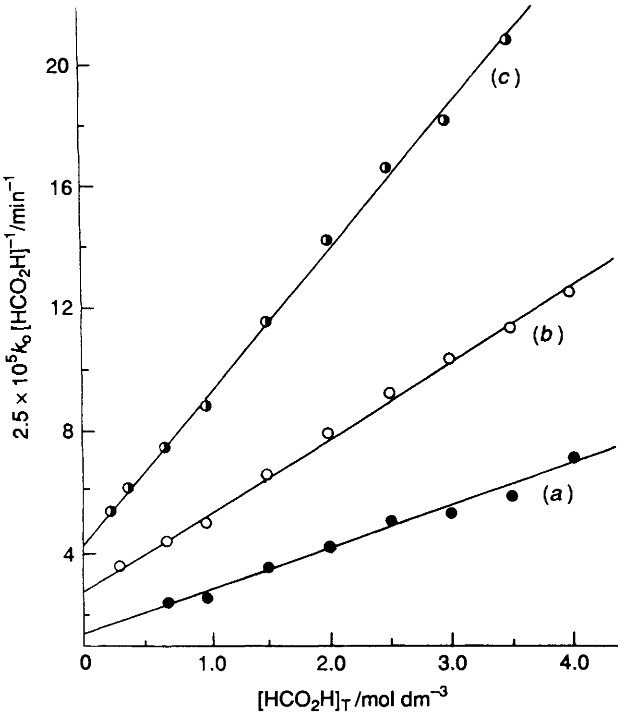

Fig. 3 Effect of formic acid on k_0 in its oxidation by cerium(IV) in the presence of ruthenium(III); $[Ce^{IV}] = 4 \times 10^{-3}$ mol dm^{-3}, $[Ru^{III}] = 3 \times 10^{-6}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $I = 2.75$ mol dm^{-3}; T = 30 (*a*), 40 (*b*) or 50 °C (*c*)

Acrylonitrile Polymerisation Test.—No polymerisation was observed when acrylonitrile was added to the reaction mixture under a nitrogen atmosphere. This indicates that free radicals are not generated or that free radicals are removed by a reactant before they can initiate polymerisation during the course of reaction. Here it is worth mentioning that in absence of the catalyst (*i.e.* Ru^{III}), addition of acrylonitrile under identical conditions led to the reaction mixture becoming viscous indicating formation of free radicals.

Mechanism of the Reaction.—The reaction follows zero-order kinetics with respect to cerium(IV) indicating the absense of cerium(IV) in the rate-determining steps. Thus it is reasonable[26b,30b,40] to consider that the catalyst alone participates in the electron-transfer process involving formic acid followed by the regeneration of the catalyst by cerium(IV) in a fast step. The detection of carbon dioxide from a reaction solution containing ruthenium(III) and excess formic acid in 1.0 mol dm^{-3} sulfuric acid kept on a boiling water bath is in agreement with this argument. To explain the absence of free radical generation, it is reasonable to propose that the catalyst acts as a two-electron acceptor through a ruthenium(III)–ruthenium(I) cycle. In fact, in many cases,[26b,f,40] ruthenium(III) has been found to act as a two-electron acceptor in catalytic cycles. In the present system, it is believed that Ru^{III}–Ru^{III}H cycle operates and Ru^{III}H is formed by the abstraction of hydride from the C–H bond of the substrate. A large number of ruthenium hydride complexes are now well characterised.[41] Such hydride-ion transfer mechanism in ruthenium(III) catalysis is proposed[26b,40,41e,f] in the oxidation of different organic substrates. Considering the acid dissociation constant (K_a) of formic acid and hydrolysis constant (K_h) of the catalyst, the following reactions (5)–(23) are

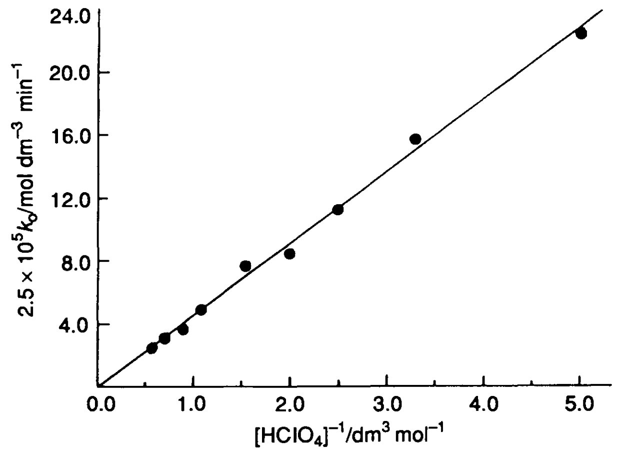

Fig. 4 Effect of [H$^+$] on k_0 for the oxidation of formic acid by cerium(IV) in the presence of ruthenium(III); $[Ce^{IV}] = 4 \times 10^{-3}$ mol dm^{-3}, $[Ru^{III}] = 3 \times 10^{-6}$ mol dm^{-3}, $[HCO_2H] = 1.0$ mol dm^{-3}, $[NaHSO_4] = 1.0$ mol dm^{-3}, $I = 2.75$ mol dm^{-3}, 40 °C

$$Ru^{III} \underset{}{\overset{K_h}{\rightleftharpoons}} Ru^{III}(OH) + H^+ \qquad (5)$$

$$HCO_2H \overset{K_a}{\rightleftharpoons} HCO_2^- + H^+ \qquad (6)$$

$$Ru^{III} + HCO_2H \overset{K_1}{\rightleftharpoons} Ru^{III}(HCO_2H) \qquad (7)$$

$$Ru^{III}(HCO_2H) \overset{K_2}{\rightleftharpoons} Ru^{III}(HCO_2^-) + H^+ \qquad (8)$$

$$Ru^{III} + HCO_2^- \overset{K_2'}{\rightleftharpoons} Ru^{III}(HCO_2^-) \qquad (9)$$

$$Ru^{III}(OH) + HCO_2H \overset{K_2''}{\rightleftharpoons} Ru^{III}(HCO_2^-) \qquad (10)$$

$$Ru^{III}(HCO_2H) + HCO_2H \overset{K_3}{\rightleftharpoons} Ru^{III}(HCO_2H)_2 \qquad (11)$$

$$Ru^{III}(HCO_2H)_2 \overset{K_4}{\rightleftharpoons} Ru^{III}(HCO_2H)(HCO_2^-) + H^+ \qquad (12)$$

$$\mathrm{Ru^{III}(HCO_2H) + HCO_2^-} \overset{K_4'}{\rightleftharpoons} \mathrm{Ru^{III}(HCO_2H)(HCO_2^-)} \quad (13)$$

$$\mathrm{Ru^{III}(HCO_2^-) + HCO_2H} \overset{K_4''}{\rightleftharpoons} \mathrm{Ru^{III}(HCO_2H)(HCO_2^-)} \quad (14)$$

$$\mathrm{Ru^{III}(HCO_2H)(HCO_2^-)} \overset{K_5}{\rightleftharpoons} \mathrm{Ru^{III}(HCO_2^-)_2 + H^+} \quad (15)$$

$$\mathrm{Ru^{III}(HCO_2^-) + HCO_2^-} \overset{K_5'}{\rightleftharpoons} \mathrm{Ru^{III}(HCO_2^-)_2} \quad (16)$$

$$\mathrm{Ru^{III}(HCO_2H)_2} \overset{K_5''}{\rightleftharpoons} \mathrm{Ru^{III}(HCO_2^-)_2 + 2H^+} \quad (17)$$

$$\mathrm{Ru^{III}(HCO_2H)} \xrightarrow{k_1} \mathrm{Ru^{III}H + CO_2 + H^+} \quad (18)$$

$$\mathrm{Ru^{III}(HCO_2^-)} \xrightarrow{k_2} \mathrm{Ru^{III}H + CO_2} \quad (19)$$

$$\mathrm{Ru^{III}(HCO_2H)_2} \xrightarrow{k_3} \mathrm{Ru^{III}H + CO_2 + H^+ + HCO_2H} \quad (20)$$

$$\mathrm{Ru^{III}(HCO_2H)(HCO_2^-)} \xrightarrow{k_4} \mathrm{Ru^{III}H + CO_2 + HCO_2H} \quad (21)$$

$$\mathrm{Ru^{III}(HCO_2^-)_2} \xrightarrow{k_5} \mathrm{Ru^{III}H + CO_2 + HCO_2^-} \quad (22)$$

$$\mathrm{Ru^{III}H + 2Ce^{IV}} \xrightarrow{\text{fast}} \mathrm{Ru^{III} + H^+ + 2Ce^{III}} \quad (23)$$

proposed incorporating the various possible species of formic acid both in the bulk solvent and in the co-ordination sphere of the catalyst. That the formic acid undergoes complexation with ruthenium(III) has been verified by observing the spectral changes of the pre-equilibrated solutions containing ruthenium(III) and formic acid. At fixed acidity and ruthenium concentration, the absorbance at 295 nm [λ_{max} of ruthenium(III)] decreases with increasing formic acid concentration. To explain both the first-order (k_b) and second-order (k_c) path with respect to formic acid, both mono- and bis-complexes are suggested to exist.

Considering all the pre-equilibria (5)–(17) to be established rapidly compared with the reactions (18)–(22) and the various alternative pathways for the formation of each complex kinetically indistinguishable [*e.g.* $\mathrm{Ru^{III}(HCO_2^-)}$ is formed *via* either reactions (7) and (8) or reactions (6) and (9) or reactions (5) and (10)], the rate of disappearance of total cerium(IV) is given by equation (24). Equation (25) is one of the expressions

$$-\frac{\mathrm{d[Ce^{IV}]}}{\mathrm{d}t} = 2k_1[\mathrm{Ru^{III}(HCO_2H)}] + 2k_2[\mathrm{Ru^{III}(HCO_2^-)}] + 2k_3[\mathrm{Ru^{III}(HCO_2H)_2}] + 2k_4[\mathrm{Ru^{III}(HCO_2H)(HCO_2^-)}] + 2k_5[\mathrm{Ru^{III}(HCO_2^-)_2}] \quad (24)$$

$$-\frac{\mathrm{d[Ce^{IV}]}}{\mathrm{d}t} = k_0 = \frac{2[\mathrm{Ru}]_\mathrm{T}\{A[\mathrm{HCO_2H}]_\mathrm{T} + B[\mathrm{HCO_2H}]_\mathrm{T}{}^2\}}{(1 + K_\mathrm{h}[\mathrm{H^+}]^{-1}) + C[\mathrm{HCO_2H}]_\mathrm{T} + D[\mathrm{HCO_2H}]_\mathrm{T}{}^2} \quad (25)$$

which can be derived for the rate and which accounts for the observed variation of rate with $[\mathrm{H^+}]$, $[\mathrm{HCO_2H}]_\mathrm{T}$ and $[\mathrm{Ru}]_\mathrm{T}$ (where $[\mathrm{HCO_2H}]_\mathrm{T} \gg [\mathrm{Ru}]_\mathrm{T}$, $A = K_1(k_1 + k_2K_2[\mathrm{H^+}]^{-1})$, $B = K_1K_3(k_3 + k_4K_4[\mathrm{H^+}]^{-1} + k_5K_4K_5[\mathrm{H^+}]^{-2})$, $C = K_1(1 + K_2[\mathrm{H^+}]^{-1})$ and $D = K_1K_3(1 + K_4[\mathrm{H^+}]^{-1} + K_4K_5[\mathrm{H^+}]^{-2})$.

It should be noted that the k_4 path, instead of involving the mixed-ligand complex, $\mathrm{Ru^{III}(HCO_2H)(HCO_2^-)}$ may instead involve a kinetically indistinguishable, base catalysed reaction of $\mathrm{Ru^{III}(HCO_2H)}$ [equation (26)]. In equation (25), if

$$\mathrm{Ru^{III}(HCO_2H) + HCO_2^-} \xrightarrow{k} \mathrm{Ru^{III}H + CO_2 + HCO_2H} \quad (26)$$

$1 + K_\mathrm{h}[\mathrm{H^+}]^{-1} \gg C[\mathrm{HCO_2H}]_\mathrm{T} + D[\mathrm{HCO_2H}]_\mathrm{T}{}^2$, then k_0 is given by equation (27) which can explain the observation

$$k_0/[\mathrm{Ru}]_\mathrm{T}[\mathrm{HCO_2H}]_\mathrm{T} = \frac{2A + 2B[\mathrm{HCO_2H}]_\mathrm{T}}{1 + K_\mathrm{h}[\mathrm{H^+}]^{-1}} \quad (27)$$

given by the equation (3). Here, as the rate does not level off with increasing formic acid concentration, it is reasonable to assume that complex formation is slight. Equation (27) can be rearranged as follows [equation (28)] where $P =$

$$k_0 = \frac{2[\mathrm{Ru}]_\mathrm{T}\{P + Q[\mathrm{H^+}]^{-1} + R[\mathrm{H^+}]^{-2}\}}{1 + K_\mathrm{h}[\mathrm{H^+}]^{-1}} \quad (28)$$

$K_1[\mathrm{HCO_2H}]_\mathrm{T}\{k_1 + k_3K_3[\mathrm{HCO_2H}]_\mathrm{T}\}$, $Q = K_1[\mathrm{HCO_2H}]_\mathrm{T}\text{-}\{k_2K_2 + k_4K_3K_4[\mathrm{HCO_2H}]_\mathrm{T}\}$ and $R = k_5K_1K_3K_4K_5\text{-}[\mathrm{HCO_2H}]_\mathrm{T}{}^2$. If, $Q[\mathrm{H^+}]^{-1} \gg P + R[\mathrm{H^+}]^{-2}$ and $1 \gg K_\mathrm{h}[\mathrm{H^+}]^{-1}$ then equation (28) is reduced to equation (29) which can explain

$$k_0 = 2[\mathrm{Ru}]_\mathrm{T}Q[\mathrm{H^+}]^{-1} = 2[\mathrm{Ru}]_\mathrm{T}K_1\{k_2K_2[\mathrm{HCO_2H}]_\mathrm{T} + k_4K_3K_4[\mathrm{HCO_2H}]_\mathrm{T}{}^2\}[\mathrm{H^+}]^{-1} \quad (29)$$

the experimental observations given by equation (4).

Comparing equations (2)–(4) and (29), we obtain the following expressions for k_a, k_b, k_c and y [equations (30)–(33)].

$$k_a = 2K_1[\mathrm{HCO_2H}]_\mathrm{T}\{k_2K_2 + k_4K_3K_4[\mathrm{HCO_2H}]_\mathrm{T}\}[\mathrm{H^+}]^{-1} \quad (30)$$

$$k_b = 2k_2K_1K_2[\mathrm{H^+}]^{-1} \quad (31)$$

$$k_c = 2k_4K_1K_3K_4[\mathrm{H^+}]^{-1} \quad (32)$$

$$y = 2K_1[\mathrm{HCO_2H}]_\mathrm{T}\{k_2K_2 + k_4K_3K_4[\mathrm{HCO_2H}]_\mathrm{T}\} = [\mathrm{HCO_2H}]_\mathrm{T}\{k_b[\mathrm{H^+}] + k_c[\mathrm{H^+}][\mathrm{HCO_2H}]_\mathrm{T}\} \quad (33)$$

By using the values of k_b and k_c determined (Table 1) from the variation of formic acid concentration in 1 mol dm^{-3} sulfuric acid, the calculated value [equation (33)] of y is *ca.* 11.5 × 10^{-2} mol dm^{-3} s^{-1} which is close to the experimentally observed value [= 10.0 × 10^{-2} mol dm^{-3} s^{-1}, *cf.* Fig. 4 and equation (4)] obtained from the variation of $[\mathrm{HClO_4}]$ at constant $[\mathrm{HCO_2H}]_\mathrm{T}$ and $[\mathrm{NaHSO_4}]$. This agreement supports the validity of the proposed reaction scheme. From the activation parameters *i.e.* $\Delta H^‡$ and $\Delta S^‡$ (Table 1) of k_b and k_c, it is found that the $\Delta S^‡$ values are highly negative which predicts the rigidity of the stereochemical orientation required in the transition state for the hydride transfer.

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