KINETICS AND MECHANISM OF OXIDATION OF FORMIC ACID BY CHROMIUM(VI). INHIBITION BY MANGANESE(II) ION

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Experiments have been done to clarify the mechanism of the chromium(VI)–formic acid reaction in aqueous perchloric acid media, both in the absence and in the presence of manganese(II) ion. Two mechanisms are proposed, one for slightly acid solutions (*I*) and the other for strongly acid ones (*II*). Both mechanisms are first order in both oxidant and reductant, but they differ in the order to hydrogen ion (1 for mechanism *I* and 3 for mechanism *II*). The activation energy for mechanism *I* (60.4 ± 0.9 kJ mol^{-1}) is considerably higher than that for mechanism *II* (41.2 ± 0.4 kJ mol^{-1}). The rate-controlling steps proposed for mechanisms *I* and *II* are the H_2CrO_4–HCOOH and $HCrO_3^+$–$HCOOH_2^+$ reactions, respectively. Mechanism *I* is inhibited by manganese(II) ion, but mechanism *II* is not, which suggests that mechanism *I* involves Cr(IV) as an intermediate, whereas mechanism *II* does not.

Formic acid differs from other monocarboxylic acids because of its relatively strong reducing properties[1]. Consequently, the oxidation of formic acid by different oxidants has attracted considerable interest. In particular, the reaction between chromium(VI) and formic acid has been the objective of kinetic study for several decades[2-11].

On the other hand, manganese(II) ion has a peculiar effect on many redox processes similar to the title reaction. In the first place, it can act as a catalyst, as it does in the permanganate oxidation of formic acid[12] and also in the chromium(VI) oxidations of oxalic acid and other carboxylic acids[13,14]. In the second place, it can act as an inhibitor, as it does in the chromium(VI) oxidations of formaldehyde[15] and other organic compounds[16-18].

We have reinvestigated the kinetics of the title reaction with two main objectives: to obtain the pH-independent activation parameters associated with the true rate constants and to study the effect of manganese(II) ion on the reaction. The results are discussed in this article.

EXPERIMENTAL

The solvent used was twice-distilled water. The reductant (formic acid) was always in great excess with respect to oxidant (potassium dichromate). The pH and ionic strength of the solutions were controlled by addition of perchloric acid and sodium perchlorate (the latter only when necessary), respectively. The inhi-

bition experiments were done using manganese(II) sulfate as an additive. Other additives used were $AgNO_3$, $Cr(NO_3)_3$, $CoSO_4$, $CuSO_4$, $NiSO_4$ and $FeNH_4(SO_4)_2$. All of the reagents used were supplied by Merck (analytical grade).

The reaction was followed by monitoring the disappearance of chromium(VI) at 352 nm with a Varian Cary 219 UV-VIS spectrophotometer. Quartz cuvettes (pathlength 1 cm) were placed in the thermostated compartment of the spectrophotometer. In order to decrease experimental errors in the determination of the rate constants, room temperature was kept as close as possible (average difference 0.7 °C). This precaution was especially important in the determination of the activation parameters.

RESULTS

Non-Inhibited Reaction

The experiments done revealed that formic acid was not capable of reducing chromium(VI) in neutral solutions. On the contrary, the reaction took place in perchloric acid media, according to the following stoichiometry (Eq. (*A*)).

$$2\ HCrO_4^- + 3\ HCOOH + 8\ H^+ \rightarrow 2\ Cr^{3+} + 3\ CO_2 + 8\ H_2O \qquad (A)$$

The first-order rate plots were linear in all of the cases. The average linear correlation coefficient for the first-order rate plots corresponding to 400 kinetic runs done was 0.99998 ± 0.00001. From the slopes of those plots the values of the first-order rate constant (k_1) were obtained; for each k_1 value two independent determinations were done, the average standard deviation (0.7 ± 0.4%) indicating a good reproducibility of the rate constants.

As shown in Table I, the initial rate was directly proportional to the initial concentration of chromium(VI), confirming that the reaction was first order in the oxidant (Eq. (*1*)).

$$r = k_1\,[\mathrm{Cr(VI)}] \qquad (1)$$

TABLE I

Initial rates r_0 and first-order rate constants k_1 at various chromium(VI) concentrations ([HCOOH] = 0.530 mol dm^{-3}, [$HClO_4$] = 0.731 mol dm^{-3}, I = 0.731 mol dm^{-3}, 25.0 °C)

$[Cr(VI)]_0 \cdot 10^4$ mol dm^{-3}	$r_0 \cdot 10^{8\,a}$ mol dm^{-3} s^{-1}	$k_1 \cdot 10^{4\,b}$ s^{-1}
3.20	3.35 ± 0.02	1.047 ± 0.006
5.59	5.83 ± 0.03	1.043 ± 0.005
7.99	8.23 ± 0.06	1.030 ± 0.008
10.39	10.50 ± 0.02	1.011 ± 0.002
12.78	12.71 ± 0.15	0.995 ± 0.012

[a] $\log r_0 = -(4.10 \pm 0.03) + (0.964 \pm 0.009) \log [Cr(VI)]_0$. [b] Calculated as $k_1 = r_0 / [Cr(VI)]_0$.

Actually, a very slight decrease in k_1 with increasing $[Cr(VI)]_0$ can be detected in Table I when k_1 is obtained as the ratio $r_0 / [Cr(VI)]_0$, but this effect is indeed of minor importance. The fact that k_1 was directly proportional to [HCOOH], as shown in Fig. 1 for two different experimental situations, indicated that the reaction was also first order in the reductant (Eq. (*2*)),

$$k_1 = k_2 [HCOOH], \qquad (2)$$

k_2 being the second-order rate constant.

The reaction was accelerated by addition of sodium perchlorate to increase the ionic strength of the solution (Table II). Consequently, in the experiments done to study the effect of the acidity of the medium the ionic strength was kept constant by addition of sodium perchlorate ($[HClO_4] + [NaClO_4]$ = constant); this study was done for different experimental situations and the results indicated that in all of the cases the reaction rate increased with increasing acidity (see Fig. 2 for two typical examples).

The effect of temperature on the reaction rate was studied at five concentrations of perchloric acid, and in the five cases the first-order rate constant fulfilled the Arrhenius equation (Fig. 3). From the slopes of those plots the corresponding activation energies were obtained, and a decrease in the activation energy with increasing perchloric acid

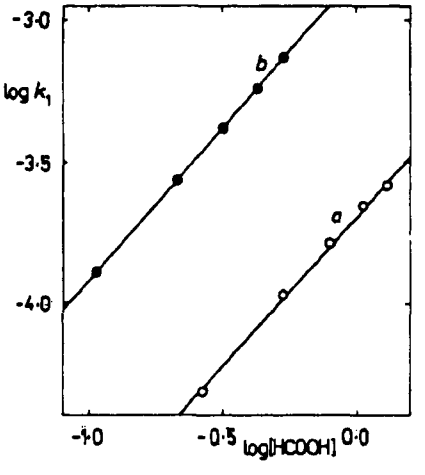

FIG. 1

Dependence of the first-order rate constant k_1 (s^{-1}) on the concentration of formic acid for its oxidation by chromium(VI) ($8.00 \cdot 10^{-4}$ mol dm^{-3}) at 25.0 °C. $[HClO_4]$ = 0.731 mol dm^{-3}, I = 0.731 mol dm^{-3}, slope = 1.06 ± 0.03 (*a*); $[HClO_4]$ = 1.757 mol dm^{-3}, I = 1.757 mol dm^{-3}, slope = 1.08 ± 0.01 (*b*)

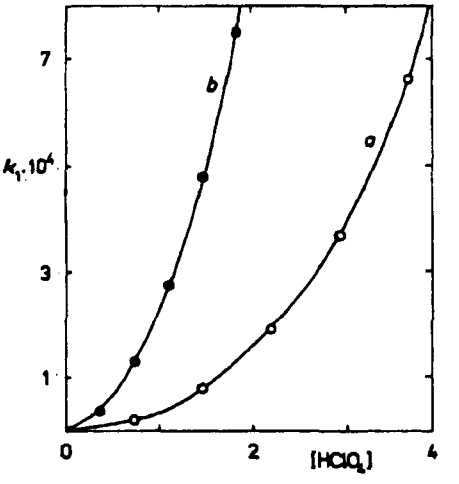

FIG. 2

Dependence of the first-order rate constant k_1 (s^{-1}) on the perchloric acid concentration (mol dm^{-3}) for the oxidation of formic acid by chromium(VI) ($8.00 \cdot 10^{-4}$ mol dm^{-3}) at 25.0 °C. [HCOOH] = $5.30 \cdot 10^{-2}$ mol dm^{-3}, I = 3.66 mol dm^{-3} ($NaClO_4$) (*a*); [HCOOH] = 0.530 mol dm^{-3}, I = 1.83 mol dm^{-3} ($NaClO_4$) (*b*)

concentration was observed (Table III). Since a true activation energy cannot depend on the acidity of the medium, the activation energies associated with the first-order rate constant were only apparent values.

In order to obtain the true activation parameters, k_1 was decomposed into the following terms (Eq. (3)),

$$k_1 = (k_3[H^+] + k_5[H^+]^3)\,[HCOOH] \qquad (3)$$

k_3 and k_5 being the true rate constants (orders 3 and 5, respectively). Equation (3) was in good agreement with the variation observed in k_1 with changing perchloric acid concentration (Fig. 2). Actually, the contribution of a mechanism of third order in hydrogen ion has also been reported for the permanganate oxidation of formic acid in perchlorid acid media[12].

Therefore, the true activation parameters were those associated with k_3 and k_5; these rate constants fulfilled the Arrhenius equation and the corresponding activation parameters are shown in Table IV. It can be seen that the decrease observed in the activation energy associated with k_1 with increasing $[HClO_4]$ (Table III) was due to the fact

TABLE II
First-order rate constants k_1 (s^{-1}) at various sodium perchlorate concentrations (in mol dm^{-3}). Conditions: $[Cr(VI)]_0 = 8.00 \cdot 10^{-4}$ mol dm^{-3}, [HCOOH] = 0.530 mol dm^{-3}, $[HClO_4]$ = 0.731 mol dm^{-3}, I = 0.73 + $[NaClO_4]$ (mol dm^{-3}), 25.0 °C

$[NaClO_4]$	$k_1 \cdot 10^4$
0.00	1.05 ± 0.01
0.73	1.18 ± 0.01
1.46	1.48 ± 0.02
2.19	1.96 ± 0.01
2.92	2.61 ± 0.02

TABLE III
Apparent activation energies E_a (kJ mol^{-1}) at various perchloric acid concentrations (in mol dm^{-3})

$[HClO_4]$	E_a
0.73	54.9 ± 0.4
1.46	50.6 ± 0.8
2.19	47.8 ± 0.8
2.92	45.8 ± 0.6
3.66	43.3 ± 0.4

that the activation energy corresponding to the mechanism predominant in the low-acidity region (rate constant k_3, E_a = 60.4 ± 0.9 kJ mol^{-1}) was higher than the one corresponding to the mechanism predominant in the high-acidity region (rate constant k_5, E_a = 41.2 ± 0.4 kJ mol^{-1}). Moreover, the apparent activation energies associated with k_1 (Table III) all are within the range given by the limits corresponding to the true activation energies (60.4 – 41.2 kJ mol^{-1}), since both of them contribute to each apparent activation energy, their respective contributions depending on the acidity of the medium.

Inhibited Reaction

Addition of manganese(II) sulfate to the solution resulted in a notable decrease of the reaction rate. As can be seen in Table V for a typical example, the reaction was very sensitive to small concentrations of $MnSO_4$, since a concentration of 7 . 10^{-6} mol dm^{-3} was enough to attain a 20% of inhibition, as determined by the corresponding decrease

TABLE IV
Activation parameters associated with the true rate constants

Rate constant	E_a kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$-\Delta S^{\neq}$ [a] J K^{-1} mol^{-1}
k_3	60.4 ± 0.9	57.9 ± 0.9	114 ± 3
k_5	41.2 ± 0.4	38.8 ± 0.4	185 ± 1

[a] The activation entropies are referred to the 1 mol dm^{-3} standard state.

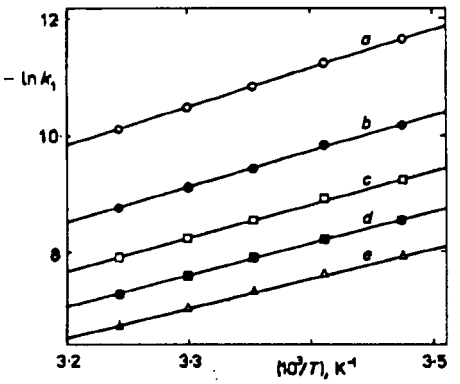

FIG. 3
Arrhenius plots for the first-order rate constant k_1 (s^{-1}) in the oxidation of formic acid (5.30 . 10^{-2} mol dm^{-3}) by chromium(VI) (8.00 . 10^{-4} mol dm^{-3}) at ionic strength 3.66 mol dm^{-3} ($NaClO_4$). [$HClO_4$], mol dm^{-3}: 0.73 (*a*), 1.46 (*b*), 2.19 (*c*), 2.92 (*d*), 3.66 (*e*)

in k_1 (that concentration was around 10^2 times smaller than the initial oxidant concentration and around 10^5 times smaller than both the reductant and perchloric acid concentrations). However, the reaction could not be completely inhibited, for an asymptotic value of k_1 was obtained when the concentration of $MnSO_4$ increased enough; for the example shown in Table V, the asymptotic value of k_1 was reached for an inhibitor concentration of around $5 \cdot 10^{-5}$ mol dm^{-3}.

The decrease in k_1 with increasing [$MnSO_4$] approximately conformed to the following law (Eq. (*4*)),

$$k_1 = a / (1 + b\,[MnSO_4]) + c, \qquad (4)$$

where *a*, *b* and *c* are empiric parameters to be obtained for every set of experimental conditions.

Excellent first-order rate plots were obtained for the reaction in the presence of manganese(II) sulfate, indicating that the inhibited reaction also was first order in the oxidant. On the other hand, the variation of parameters *a*, *b* and *c* from Eq. (*4*) with the formic acid concentration indicated that whereas both parameters *a* and *c* were directly proportional to the reductant concentration, parameter *b* was inversely proportional to it (Fig. 4). It is also interesting to notice that the concentration of $MnSO_4$ necessary to cause a given degree of inhibition (20% for instance) increased linearly with the concentration of formic acid present in the solution (Fig. 5).

TABLE V

First-order rate constants k_1 (s^{-1}) at various manganese(II) sulfate concentrations (in mol dm^{-3}). Conditions: $[Cr(VI)]_0 = 8.00 \cdot 10^{-4}$ mol dm^{-3}, [HCOOH] = 0.530 mol dm^{-3}, [$HClO_4$] = 0.731 mol dm^{-3}, I = 0.731 mol dm^{-3}, 25.0 °C

$[MnSO_4] \cdot 10^5$	$k_1 \cdot 10^5$
0.00	10.59 ± 0.12
0.24	9.70 ± 0.01
0.47	8.90 ± 0.14
0.71	8.41 ± 0.01
0.94	7.94 ± 0.03
1.18	7.62 ± 0.06
2.35	6.54 ± 0.03
3.53	6.24 ± 0.03
4.71	6.00 ± 0.10
29.41	6.16 ± 0.07
58.82	6.16 ± 0.03
88.23	6.21 ± 0.01
117.63	6.07 ± 0.01

The maximum percentage of inhibition caused by $MnSO_4$ could be obtained from the asymptotic region of the k_1 vs $[MnSO_4]$ dependence (Table V). The results indicated that the maximum percentage of inhibition was fairly independent of the formic acid concentration (Table VI), whereas it decreased notably with increasing concentration of perchloric acid (Table VII).

By application of Eq. (*3*) to the first-order rate constants of both the non-inhibited ($[MnSO_4] = 0$, $k_1 = a + c$) and inhibited ($[MnSO_4] = \infty$, $k_1 = c$) reactions, the corresponding values of rate constants k_3 and k_5 were obtained (Table VIII). It can be seen that the k_3 value of the non-inhibited reaction was twice as high as that of the inhibited one, whereas the k_5 values of the non-inhibited and inhibited reactions were of the same order of magnitude.

Finally, some experiments were done using electrolytes containing cations other than manganese(II) ion as additives; $AgNO_3$, $Cr(NO_3)_3$, $CoSO_4$, $CuSO_4$, $NiSO_4$ and $FeNH_4(SO_4)_2$. All failed to show any effect on the reaction rate in the extremely-diluted concentration range used in the inhibition experiments. As can be seen in Table IX, the inhibition effect was also present in reaction mixtures containing a constant concentration of sulfate ion ($[MnSO_4] + [CoSO_4]$ = constant), provided that $MnSO_4$ was added to the solutions. From these experiments it could be deduced that the inhibition effect was caused by manganese(II) ion and not by sulfate ion, and also that the inhibition effect on the chromium(VI)–formic acid reaction seemed to be rather specific of manganese(II) ion.

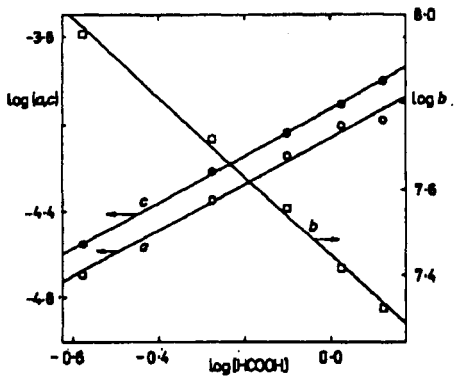

FIG. 4

Dependence of parameters *a*, *b* and *c* on the concentration of formic acid for its oxidation by chromium(VI) ($8.00 \cdot 10^{-4}$ mol dm^{-3}) in the presence of perchloric acid (0.731 mol dm^{-3}) at ionic strength 0.731 mol dm^{-3} and 25.0 °C. Parameter *a*: slope = 1.06 ± 0.07; parameter *b*: slope = −0.91 ± 0.04; parameter *c*: slope = 1.07 ± 0.01

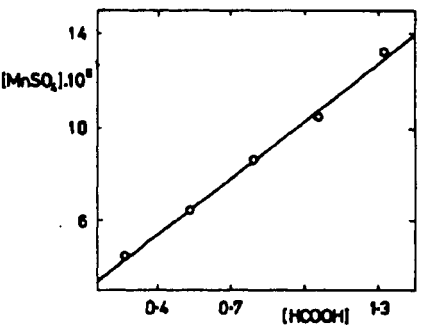

FIG. 5

Dependence of the concentration of manganese(II) sulfate (in mol dm^{-3}) necessary to cause a 20% of inhibition on the concentration of formic acid (in mol dm^{-3}) for its oxidation by chromium(VI) ($8.00 \cdot 10^{-4}$ mol dm^{-3}) in the presence of perchloric acid (0.731 mol dm^{-3}) at ionic strength 0.731 mol dm^{-3} and 25 °C

DISCUSSION

Non-Inhibited Reaction

As far as the reaction in the absence of manganese(II) ion is concerned, two mechanisms can be proposed, one for the low-acidity region:

$$HCrO_4^- + H^+ \leftrightarrow H_2CrO_4 \qquad (B)$$

$$H_2CrO_4 + HCOOH \rightarrow H_2CrO_3 + CO_2 + H_2O \qquad (C)$$

$$H_2CrO_3 + HCOOH \rightarrow H_2CrO_2 + CO_2 + H_2O \qquad (D)$$

$$H_2CrO_4 + H_2CrO_2 \rightarrow HCrO_3 + HCrO_2 + H_2O \qquad (E)$$

$$HCrO_3 + HCOOH \rightarrow HCrO_2 + CO_2 + H_2O \qquad (F)$$

$$HCrO_2 + H_2O \rightarrow Cr^{3+} + 3\,OH^- \qquad (G)$$

and the other for the high-acidity region:

$$H_2CrO_4 + H^+ \leftrightarrow HCrO_3^+ + H_2O \qquad (H)$$

$$HCOOH + H^+ \leftrightarrow HCOOH_2^+ \qquad (I)$$

TABLE VI

Maximum percentages of inhibition caused by manganese(II) sulfate at various formic acid concentrations (in mol dm^{-3}). Conditions: $[Cr(VI)]_0 = 8.00 \cdot 10^{-4}$ mol dm^{-3}, $[HClO_4] = 0.731$ mol dm^{-3}, $I = 0.731$ mol dm^{-3}, 25.0 °C

[HCOOH]	Inhibition, %
0.27	42.6 ± 0.9
0.53	42.9 ± 1.2
0.80	43.9 ± 0.6
1.06	44.2 ± 0.4
1.33	39.9 ± 0.7

$$HCrO_3^+ + HCOOH_2^+ \rightarrow HCrO_3 + HCOO^\bullet + 2\,H^+ \qquad (J)$$

$$HCrO_3^+ + HCOO^\bullet \rightarrow HCrO_3 + CO_2 + H^+ \qquad (K)$$

Once formed $HCrO_3$ through the latter mechanism in Eqs (*J*) and (*K*), it would be reduced by formic acid to $HCrO_2$ as in Eq. (*F*), and the latter would react with the solvent as in Eq. (*G*) to give Cr^{3+}.

According to the mechanisms given by Eqs (*B*) – (*K*) , the total reaction rate is given by Eq. (*5*),

$$r = -d[Cr(VI)]/dt = (k_C\,[HCOOH] + k_E\,[H_2CrO_2])\,[H_2CrO_4] + \\ + (k_J\,[HCOOH_2^+] + k_K[HCOO^\bullet])\,[HCrO_3^+], \qquad (5)$$

where k_C, k_E, k_J and k_K are the rate constants corresponding to Eqs (*C*), (*E*), (*J*) and (*K*), respectively.

The concentrations of the intermediates appearing in Eq. (*5*) can be written as

$$[H_2CrO_4] = K_B\,[HCrO_4^-][H^+] \qquad (6)$$

$$[HCrO_3^+] = K_B K_H\,[HCrO_4^-][H^+]^2 \qquad (7)$$

$$[HCOOH_2^+] = K_I\,[HCOOH][H^+] \qquad (8)$$

$$[H_2CrO_2] = k_C\,[HCOOH]/k_E \qquad (9)$$

TABLE VII

Maximum percentages of inhibition caused by manganese(II) sulfate at various perchloric acid concentrations (in mol dm^{-3}). Conditions: $[Cr(VI)]_0 = 8.00 \cdot 10^{-4}$ mol dm^{-3}, [HCOOH] = 0.530 mol dm^{-3}, I = 1.83 mol dm^{-3} ($NaClO_4$), 25.0 °C

$[HClO_4]$	Inhibition, %
0.37	47.5 ± 0.4
0.73	40.3 ± 1.2
1.10	34.8 ± 0.8
1.46	29.6 ± 0.8
1.83	26.3 ± 0.5

$$[HCOO^{\bullet}] = K_I k_J [HCOOH][H^+]/k_K \qquad (10)$$

where K_B, K_H and K_I are the equilibrium constants corresponding to Eqs (*B*), (*H*) and (*I*), respectively. To obtain Eqs (*6*) – (*10*) it has been considered that Eqs (*B*), (*H*) and (*I*) are equilibrium steps, as well as that the intermediates H_2CrO_3, H_2CrO_2 and $HCOO^{\bullet}$ are in steady state.

The steady-state approximation requires that the intermediates to which it is applied be very reactive, so that they are present in the system only in very low concentration. This requirement seems warranted for a free radical such as $HCOO^{\bullet}$, since its oxidation in Eq. (*K*) by the strong oxidant $HCrO_3^+$ can be assumed to be very fast. On the other hand, Cr(II) is known to be a very powerful reducing agent[19], so that the oxidation of H_2CrO_2 by chromic acid in Eq. (*E*) can also be assumed to be very fast. Albeit of the three intermediates to which the steady-state approximation has been applied H_2CrO_3 is probably the least reactive one, the Cr(IV) / Cr(II) reduction potential is extremely favorable[19]; hence, the rate constant for the reduction of H_2CrO_3 by formic acid in Eq. (*D*) to give H_2CrO_2 is probably much higher than that corresponding to its formation in Eq. (*C*) from the reduction of chromic acid by formic acid, so that the intermediate H_2CrO_3 can also be safely assumed to be in a steady state.

Substitution of Eqs (*6*) – (*10*) in Eq. (*5*) leads to the following expression for the reaction rate:

$$r = 2K_B (k_C [H^+] + K_H K_I k_J [H^+]^3) [HCrO_4^-] [HCOOH] \qquad (11)$$

and for the first-order rate constant:

$$k_1 = r / [HCrO_4^-] = 2K_B (k_C [H^+] + K_H K_I k_J [H^+]^3) [HCOOH] . \qquad (12)$$

Equations (*11*) and (*12*) are in agreement with the results found for the non-inhibited reaction, since the kinetic orders of oxidant and reductant are both unity. The slight decrease found in k_1 with increasing $[Cr(VI)]_0$ (Table I) is probably due to formation of $Cr_2O_7^{2-}$ from $HCrO_4^-$, the latter being more reactive toward HCOOH than the former. The dependence on the acidity of the medium also agrees with the experimental results (Fig. 2); a comparison of the theoretical expression for k_1 (Eq. (*12*)) with the experimental one (Eq. (*3*)) leads to the following equations for the experimental rate constants k_3 and k_5 (Eqs (*13*) and (*14*)).

$$k_3 = 2K_B k_C \qquad (13)$$

$$k_5 = 2K_B K_H K_I k_J \qquad (14)$$

On the other hand, although the ionic strength study was done at far too high values of the ionic strength for the Debye–Hückel theory to apply, the increase found in k_1 with increasing ionic strength (Table II) seems to suggest that two like-charged ions are involved in one of the rate-controlling steps, as happens in Eq. (*J*). Furthermore, according to the mechanisms proposed, the fact that the activation energy associated with k_5 is considerably smaller than that associated with k_3 (Table IV) might be related to an enhanced oxidizing power of $HCrO_3^+$ with respect to that of H_2CrO_4 (see Eqs (*13*) and (*14*)).

Finally, it should be noticed that the existence of $HCrO_3^+$ in strongly acidic media is well established[20], whereas the appearance of H_2CrO_3 as an intermediate in chromium(VI) oxidations carried out in acidic media has already been proposed[21]. Moreover, the involvement of a reaction between $HCrO_3^+$ (or its hydrated form, $H_3CrO_4^+$) and $HCOOH_2^+$ as a rate-controlling step has been proposed for the chromium(VI) oxidation of formic acid in sulfuric media[7]; as we have just seen, our results in perchloric acid media seem to be also in agreement with that assumption.

Inhibited Reaction

The participation of manganese(II) ion in the inhibited reaction might be as follows:

$$H_2CrO_3 + Mn^{2+} \rightarrow HCrO_2 + Mn^{3+} + OH^- \qquad (L)$$

$$2\,Mn^{3+} + 2\,H_2O \rightarrow Mn^{2+} + MnO_2 + 4\,H^+ \qquad (M)$$

$$MnO_2 + HCOOH \rightarrow Mn^{2+} + CO_2 + 2\,OH^- \qquad (N)$$

After formed in Eq. (*L*), the intermediate $HCrO_2$ would react with the solvent to give Cr^{3+} (Eq. (*G*)).

TABLE VIII
Rate constants k_3 ($dm^6\ mol^{-2}\ s^{-1}$) and k_5 ($dm^{12}\ mol^{-4}\ s^{-1}$) for the reactions non-inhibited and inhibited by manganese(II) sulfate ($[Cr(VI)]_0 = 8.00 \cdot 10^{-4}$ mol dm^{-3}, [HCOOH] = 0.530 mol dm^{-3}, $[HClO_4]$ = 0.37 – 1.83 mol dm^{-3}, I = 1.83 mol dm^{-3} ($NaClO_4$), 25.0 °C)

Reaction	$k_3 \cdot 10^4$	$k_5 \cdot 10^4$
Non-inhibited	2.2 ± 0.4[a]	1.8 ± 0.2[b]
Inhibited	1.1 ± 0.2[a]	1.4 ± 0.1[b]

[a] Ratio (non-inhibited / inhibited) = 2.0 ± 0.7. [b] Ratio (non-inhibited / inhibited) = 1.3 ± 0.2.

Thus, for the reaction in the presence of manganese(II) ion the concentration of the intermediate H_2CrO_2 would be as in Eq. (*15*).

$$[H_2CrO_2] = k_C\,[HCOOH] / k_E\,\{1+ (k_L / k_D\,[HCOOH])\,[Mn^{2+}]\} \qquad (15)$$

This relation has been obtained by application of the steady-state condition to the intermediates H_2CrO_3 (formed in Eq. (*C*) and consumed in Eqs (*D*) and (*L*)) and H_2CrO_2 (formed in Eq. (*D*) and consumed in Eq. (*E*)). It can be seen that Eq. (*9*) is just a particular case of Eq. (*15*) for $[Mn^{2+}] = 0$.

Hence, substitution of Eqs (*6*) – (*8*), (*10*) and (*15*) in Eq. (*5*) leads to the following expression for the reaction rate (Eq. (*16*)),

$$r = K_B\,k_C\,[HCrO_4^-][HCOOH][H^+] / \{1+(k_L / k_D\,[HCOOH])[Mn^{2+}]\} +$$

$$+ K_B\,k_C\,[HCrO_4^-][HCOOH][H^+] + 2\,K_B\,K_{II}\,K_I\,k_J\,[HCrO_4^-][HCOOH][H^+]^3 \qquad (16)$$

and for the first-order rate constant (Eq. (*17*)).

$$k_1 = K_B\,k_C\,[HCOOH]\,[H^+] / \{1+(k_L / k_D\,[HCOOH])\,[Mn^{2+}]\} +$$

$$+ K_B\,k_C\,[HCOOH]\,[H^+] + 2\,K_B\,K_H\,K_I\,k_J\,[HCOOH]\,[H^+]^3 \qquad (17)$$

A comparison of the theoretical Eq. (*17*) with the experimental Eq. (*4*) leads to the following expressions for the empiric parameters *a*, *b* and *c* (Eqs (*18*) – (*20*)).

$$a = K_B\,k_C\,[HCOOH]\,[H^+] \qquad (18)$$

$$b = k_L / k_D\,[HCOOH] \qquad (19)$$

TABLE IX

First-order rate constants k_1 (s^{-1}) at $[MnSO_4] + [CoSO_4]$ = constant ($[Cr(VI)]_0 = 8.00 \cdot 10^{-4}$ mol dm^{-3}, $[HCOOH] = 0.530$ mol dm^{-3}, $[HClO_4] = 0.731$ mol dm^{-3}, $I = 0.731$ mol dm^{-3}, 25.0 °C)

$[MnSO_4] \cdot 10^5$ [a]	$[CoSO_4] \cdot 10^5$ [a]	$k_1 \cdot 10^5$
0.00	3.07	10.47 ± 0.08
0.77	2.30	8.33 ± 0.02
1.54	1.54	7.11 ± 0.06
2.30	0.77	6.58 ± 0.01
3.07	0.00	6.22 ± 0.06

[a] In mol dm^{-3}.

$$c = (K_B k_C [H^+] + 2 K_B K_H K_I k_J [H^+]^3) [HCOOH] \quad (20)$$

Equation (*16*) is in agreement with the first order experimentally found for the oxidant in the inhibited reaction. On the other hand, Eqs (*18*) – (*20*) are also in agreement with the experimental results found in Fig. 4, for both parameters a and c are directly proportional to the formic acid concentration, whereas parameter b is inversely proportional to it.

The fact that the concentration of manganese(II) ion necessary to reach a given percentage of inhibition increases with increasing formic acid concentration (Fig. 5) is easy to explain. Effectively, according to the mechanism proposed in Eqs (*L*) – (*N*), the inhibition effect occurs due to the competition existing between HCOOH and Mn^{2+} to react with H_2CrO_3 (Eq. (*D*) vs Eq. (*L*)). When H_2CrO_3 is reduced by HCOOH, H_2CrO_2 is formed (Eq. (*D*)), the latter reacting later with H_2CrO_4 (Eq. (*E*)); on the contrary, when H_2CrO_3 is reduced by Mn^{2+} (Eq. (*L*)), H_2CrO_2 is not formed, and so the reaction between the latter and H_2CrO_4 does not occur. Therefore, it follows that the more concentrated HCOOH is, the higher will be the concentration of Mn^{2+} necessary to inhibit completely Eq. (*D*) by being substituted for Eq. (*L*).

It follows easily from Eq. (*4*) that the maximum percentage of inhibition can be calculated as follows (Eq. (*21*)),

$$\text{Inhibition (\%)} = 100\, a / (a + c), \quad (21)$$

since the values of k_1 for concentrations of $MnSO_4$ 0 and ∞ are $a + c$ and c, respectively. By substitution of Eqs (*18*) and (*20*) in Eq. (*21*) we obtain Eq. (*22*)

$$\text{Inhibition (\%)} = 50\, k_C / (k_C + K_H K_I k_J [H^+]^2) \quad (22)$$

in agreement with the experimental results, for the maximum percentage of inhibition is independent of the formic acid concentration (Table VI) and it decreases with increasing acidity of the solution (Table VII). According to Eq. (*22*), the highest value of the maximum percentage of inhibition that can be expected is 50% (for $[H^+] = 0$) and the lowest value 0% (for $[H^+] = \infty$) which explains that all the experimental values of that magnitude be within the range 0 – 50% (see Tables VI and VII).

Furthermore, considering that the k_1 value for the inhibited reaction is given by parameter c, it follows from Eqs (*3*) and (*20*) that the rate constants k_3 and k_5 for the inhibited reaction are given by Eqs (*23*) and (*24*).

$$k_3^i = K_B k_C \quad (23)$$

$$k_5^i = 2 K_B K_H K_I k_J \quad (24)$$

Equations (*23*) and (*24*) are in satisfactory agreement with the experimental results (see Table VIII), for if they are compared with Eqs (*13*) and (*14*), respectively, it can be inferred that the k_3 value for the non-inhibited reaction (Eq. (*13*)) is the double of that for the inhibited one (Eq. (*23*)), whereas the k_5 value for the non-inhibited reaction (Eq. (*14*)) is the same as that of the inhibited one (Eq. (*24*)).

Actually, the intermediate MnO_2 formed in Eq. (*M*) was detected in the inhibition experiments done in the present work, for the initially-yellow solutions took a brownish colour when all the chromium(VI) had been consumed, the latter colour being typical of colloidal manganese dioxide[22]; later, the brownish colour slowly disappeared to give a colourless solution. These observations seem to indicate that the reduction of MnO_2 by HCOOH (Eq. (*N*)) might be considerably slow.

It should be noticed that the explanation given here for the inhibition of the chromium(VI) oxidation of formic acid by manganese(II) ion is coherent with the one usually accepted in the literature[15,16,23].

On the other hand, trapping of Cr(IV) by manganese(II) ion (as in Eq. (*L*)) is known to be an useful tool to determine when Cr(IV) is involved as an intermediate in reactions of Cr(VI) with reductants[24]. This fact, along with our experimental findings, can explain why in the mechanism for the non-inhibited reaction in the low-acidity region (Eqs (*B*) – (*G*)) Cr(IV) has been postulated as an intermediate, whereas it has not been postulated as an intermediate in the mechanism for the non-inhibited reaction in the high-acidity region (Eqs (*H*) – (*K*)), since that is the easiest way to explain the decrease in the maximum percentage of inhibition with increasing perchloric acid concentration found in this work (Table VII).

Finally, it should be mentioned that in an earlier work[6] no inhibition by manganese(II) ion was found for the reaction between chromium(VI) and formic acid in perchloric acid media. According to our results, the most probable reason for that to be so might be the very high concentration of perchloric acid used in that work (3.67 mol dm^{-3}), for we can see in Table VII that the maximum percentage of inhibition that can be attained rapidly decreases as the perchloric acid concentration increases. In extremely-acid solutions (where the mechanism given by Eqs (*H*) – (*K*) would be predominant) no inhibition by manganese(II) ion would be expected, given that the reduction would follow the sequence Cr(VI) → Cr(V) → Cr(III) without passing through Cr(IV) as an intermediate.

REFERENCES

1. Ansell M. F., Gigg R. H.: *Rodd's Chemistry of Carbon Compounds*, 2nd ed., Vol. 1, Part C, p. 96. Elsevier, New York 1965.
2. Snethlage H. C. S.: Rec. Trav. Chim. *60*, 877 (1941).
3. Mahajani A. V., Bhattacharya A. K.: Proc. Natl. Acad. Sci. India, A *23*, 65 (1954).
4. Mahajani A. V.: Proc. Natl. Acad. Sci. India, A *26*, 49 (1957).
5. Pungor E., Trompler J.: J. Inorg. Nucl. Chem. *5*, 123 (1957).

6. Kemp T. J., Waters W. A.: Proc. R. Soc. London, A *274*, 480 (1963).
7. Venkatraman R., Rao S. B.: Indian J. Chem. *10*, 165 (1972).
8. Sanchez F., Rodriguez J.: Ion *33*, 570 (1973).
9. Reddy C. O., Rao S. B.: Indian J. Chem., A *15*, 1113 (1977).
10. Rodriguez J., Sanchez F.: Ion *37*, 1 (1977).
11. Mahajani A. V., Mahajani S.: J. Sci. Res. (Bhopal, India) *1*, 25 (1978).
12. Perez-Benito J. F., Arias C., Brillas E.: Int. J. Chem. Kinet. *22*, 261 (1990).
13. Kemp T. J., Waters W. A.: J. Chem. Soc. *1964*, 3193.
14. Huber C. F., Haight G. P.: J. Am. Chem. Soc. *98*, 4128 (1976).
15. Chatterji A. C., Mukherjee S. K.: J. Am. Chem. Soc. *80*, 3600 (1958); Z. Phys. Chem. (Leipzig) *210*, 255 (1959).
16. Watanabe W., Westheimer F. H.: J. Chem. Phys. *17*, 61 (1949).
17. Chatterji A. C., Antony V.: Proc. Natl. Acad. Sci. India, A *23*, 20 (1954).
18. Saran N. K., Acharya R. C.: J. Indian Chem. Soc. *62*, 747 (1985).
19. Beattie J. K., Haight G. P. in: *Inorganic Reaction Mechanisms* (J. O. Edwards, Ed.), Part II, p. 96. Wiley, New York 1972.
20. Levitt L. S.: J. Org. Chem. *20*, 1297 (1955).
21. Graham G. T. E., Westheimer F. H.: J. Am. Chem. Soc. *80*, 3030 (1958).
22. Mata F., Perez-Benito J. F.: Can. J. Chem. *63*, 988 (1985).
23. Wiberg K. B., Mill T.: J. Am. Chem. Soc. *80*, 3022 (1958).
24. Srinivasan C., Chellamani A., Rajagopal S.: J. Org. Chem. *50*, 1201 (1985).