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Oxidation of Maleatopentaamminecobalt(III) by Permanganate Ion: Evidence for an Even-electron Process

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The permanganate oxidation of maleic acid [1] and other olefinic substrates [2] in acidic media has been found to involve an initial 4-electron process, yielding manganese(III) as the first detectable intermediate. Although the original data pointed to no deviation from this behaviour, we have now investigated whether the close proximity of a cobalt(III) center, as in maleatopentaamminecobalt(III), Co(Hmal)$^{2+}$, interferes with the oxidation pattern observed for uncomplexed maleic acid. Such interference leading to induced electron transfer to cobalt(III) seemed possible by analogy to the reaction of $[(NH_3)_5CoO_2CH]^{2+}$ with MnO_4^- studied by Candlin and Halpern [3] and further explored by Taube *et al.* [4]. Their results have shown that the formation of aquacobalt(II) is diagnostic for a coordinated radical intermediate of finite lifetime. It was also of interest to compare the kinetics of maleate oxidation in the free and coordinated state. The results and main conclusions are reported in this paper.

Permanganate ion rapidly oxidizes Co(Hmal)$^{2+}$ in acidic aqueous solutions up to a mol ratio of 1:1. Permanganate added in excess of this value reacts more slowly. MnO_2 is not a product unless the pH is higher than 3 and the MnO_4^-: Co(Hmal)$^{2+}$ mol ratio is greater than 1. The MnO_4^- oxidation of Co(Hmal)$^{2+}$ is accompanied by the accumulation and decay of a short-lived intermediate detectable by stopped-flow spectrophotometry at 250 nm. It has been identified as manganese(III) on the basis of the fact that, at a reactant mol ratio of 1:1, the addition of pyrophosphate in a 5-fold excess over the initial MnO_4^- concentration eliminates the maximum on the stopped-flow trace and the resulting pink solution shows the visible spectrum of pyrophosphatomanganese(III), a much more sluggish oxidant than the aquamanganese(III) ion. Aquacobalt(II) is formed as product, which can be detected and determined as the $Co(NCS)_4^{2-}$ complex in aqueous acetone. In Fig. 1 the amount of cobalt(II) is shown as a function of the MnO_4^- concentration. At pH 0.5, the concentration of cobalt(II) formed is directly proportional to the MnO_4^- concentration, the slope being 0.3 mol Co^{2+}/mol MnO_4^- added. At higher pH's, strong negative deviations from proportionality are observed.

Cobalt(II) ions are not formed if, under otherwise identical conditions, the reaction is carried out in the presence of a 5-fold excess of pyrophosphate over the MnO_4^- added. Under such conditions, oxida-

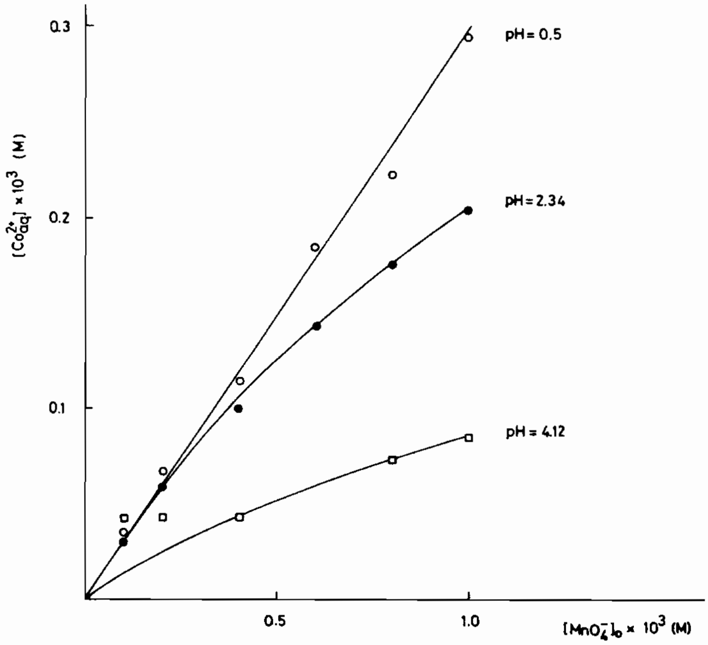
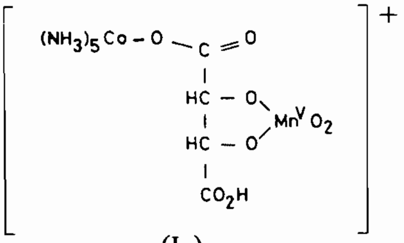


Figure 1. Dependence of the concentration of aquacobalt(II) formed on the MnO_4^- concentration. $[Co(Hmal)^{2+}]_o = 1 \times 10^{-3}$ *M*; T = 25 °C.

tion by the manganese(III) intermediate is suppressed owing to complex formation with pyrophosphate. This implies that reduction of the cobalt(III) center occurs after, rather than during the 4-electron process leading to manganese(III) formation. Consequently, the initial 4-electron process, involving two consecutive 2-electron steps, is energetically much more favourable than any sequence of 1-electron and 2-electron steps, leading to the same overall 4-electron change. Thus no radical intermediates accompany the $MnO_4^- \rightarrow Mn(III)$ transformation. This lends additional support to the mechanism proposed previously [1] for the permanganate oxidation of free maleic acid and its anions, involving near-concerted *cis*-attack of MnO_4^- on the double bond, leading to a very short-lived and undetectable manganate(V) ester, which then rapidly decomposes to manganese(III), CO_2 and formyl(hydroxy)acetic acid. For $Co(Hmal)^{2+}$ as the olefinic substrate, this mechanism is depicted by eqs. (1)–(2a). As shown by separate experiments, Mn(III) does not attack $Co(Hmal)^{2+}$ to any appreciable extent.

$$[(NH_3)_5Co{-}OCO{-}CH{=}CH{-}CO_2H]^{2+} \xrightarrow{MnO_4^-}$$



(I₁)

(1)

$$I_1 \xrightarrow[-CO_2]{\text{fast}} \underset{(I_{2a})}{[(NH_3)_5Co{-}OCO{-}CHOH{-}CHO]^{2+}} + Mn(III) \qquad (2a)$$

Decarboxylation at the coordinated carboxylate group would clearly sever the ligand to cobalt bond and thus would eliminate the possibility of induced reduction to cobalt(II) via attack of manganese(III) on I_2. By analogy to free maleic acid [5], minor contributions from a path involving C(2)–C(3) bond cleavage, leading to free and coordinated glyoxylic acid, eq. (2b), are to be expected.

$$I_1 \xrightarrow{\text{fast}} \underset{(I_{2b})}{[(NH_3)_5Co{-}OCO{-}CHO]^{2+}} + HO_2C{-}CHO + Mn(III) \qquad (2b)$$

The induced reduction of cobalt(III) presumably occurs via step (3), while step (4) represents a competitive path producing tartronatopentaamminecobalt(III). Tartronic acid was detected as a product

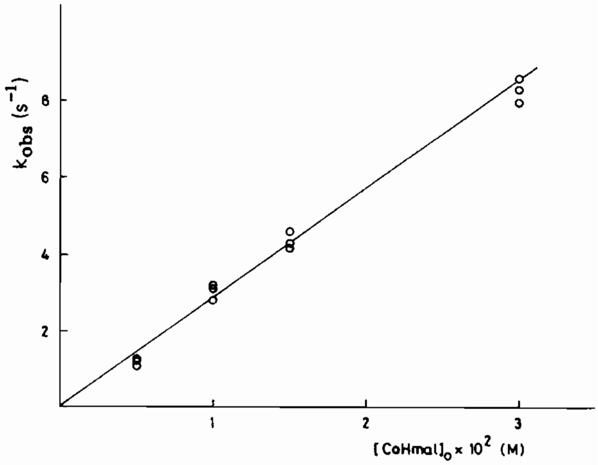


Figure 2. Dependence of k_{obs} on the initial concentration of $Co(Hmal)^{2+}$ at pH = 3.50, T = 25 °C.

with free maleic acid, derived from the manganese(III) oxidation of formyl(hydroxy)acetic acid.

$$I_{2a} \xrightarrow[-Mn(II)]{Mn(III)} \underset{(I_3)}{[(NH_3)_5Co{-}OCO{-}CHOH{-}\dot{C}O]^{2+}} \xrightarrow[H_2O]{5H^+} Co(II) + 5NH_4^+ + HO_2C{-}CHOH{-}CO_2H \qquad (3)$$

$$I_3 \xrightarrow[-Mn(II),\,-H^+]{Mn(III),H_2O} [(NH_3)_5Co{-}OCO{-}CHOH{-}CO_2H]^{2+} \qquad (4)$$

According to Fig. 1, only about 1/3 of the total cobalt is converted to Co_{aq}^{2+} via step (3), therefore, the contribution of step (4) is very considerable. With increasing pH, the disproportionation of manganese(III) becomes significant, therefore, lower amounts of Co_{aq}^{2+} are formed. Some I_{2a} should be present as a product too, because route (1)–(2a)–(4) consumes only ½ of the I_{2a} formed. The reaction of I_3 with MnO_4^- has been disregarded as processes (1–2a) and (3–4) are strongly separated in time even if no pyrophosphate is present, as evidenced by the stopped-flow traces.

In order to check the competition of paths (3) and (4), we have prepared by the procedure of ref. 6 glyoxylatopentaamminecobalt(III), $[(NH_3)_5Co{-}OCO{-}CHO]^{2+}$, a reasonable analogue of I_{2a}, and have studied its reaction with aquamanganese(III) in 1 *M* H_2SO_4. At equal reactant concentrations of 3×10^{-3} *M*, Mn(III) disappears within 2 sec and again 1/3 of cobalt(III) is converted to Co_{aq}^{2+}. Apparently, the rate constants for (3) and (4) are similar to those governing the reaction of $[(NH_3)_5Co{-}OCO{-}CHO]^{2+}$ with Mn(III). Tartronatopentaamminecobalt(III), $[(NH_3)_5Co{-}OCO{-}CHOH{-}CO_2H]^{2+}$, also gives an

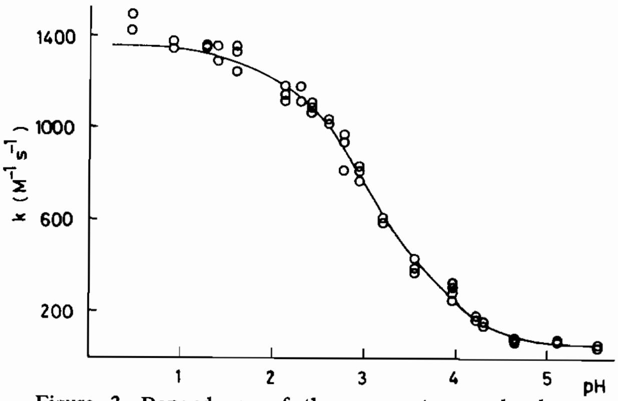


Figure 3. Dependence of the apparent second-order rate constant k on the pH at T = 25 °C.

induced reduction with manganese(III), although this is much slower.

The kinetic studies have been performed in the presence of a 10-fold excess of pyrophosphate (pyr) over MnO_4^- to suppress manganese(III) oxidations. This approach permits [1] to follow the kinetics of processes (1)–(2a, b).

Stopped-flow kinetic measurements at 540 nm have shown that at a 10-fold excess of $Co(Hmal)^{2+}$, the disappearance of MnO_4^- obeys a pseudo-first order rate law,

$$-d[MnO_4^-]/dt = k_{obs}[MnO_4^-] \quad (5)$$

and k_{obs} is proportional to the overall $Co(Hmal)^{2+}$ concentration (Fig. 2),

$$k_{obs} = k[Co(Hmal)^{2+}] \quad (6)$$

Second-order rate constant k shows a strong pH-dependence (Fig. 3), which can be ascribed to the different reactivities of the monobasic acid $Co(Hmal)^{2+}$ and its conjugate base $Co(mal)^+$. The acid dissociation constant of $Co(Hmal)^{2+}$ has been determined by pH-metric titration: pK = 3.11 ± 0.05 at 25 °C, ionic strength 1.5 M $NaClO_4$.

Assuming that the acid–base equilibrium is attained much faster than either species is consumed by MnO_4^-, the following expression can be derived for k:

$$k = \frac{k_1 a_H + k_2 K}{K + a_H} \quad (7)$$

where a_H is the hydrogen ion activity, and k_1 and k_2 are the individual rate constants for the reaction of $Co(Hmal)^{2+}$ and $Co(mal)^+$, respectively, with MnO_4^- The analysis of the experimental pH dependence of k has led to the following rate constants (25 °C, aqueous solution, ionic strength 1.5 M with $NaClO_4$, pH 0.5–5.5 adjusted with $HClO_4$ or chloroacetic acid or succinic acid buffers; $[MnO_4^-]_o = 0.5 - 3.0 \times 10^{-2}$ M, $[Co(Hmal)^{2+}]_o = 10[MnO_4^-]_o$; $[pyr]_o = 10[MnO_4^-]_o$):

$$k_1 = 1350 \pm 80\,M^{-1}\,s^{-1};\ k_2 = 61 \pm 5\,M^{-1}\,s^{-1}$$

The solid curve in Fig. 3 has been calculated using these rate constants and the pH-metric acid dissociation constant K. The observed kinetic behaviour is consistent with mechanism (1)–(2a), where step (1) is rate-determining, in full analogy to the reaction of uncomplexed maleic acid (H_2mal) [1].

It is remarkable that the reactivity of free $Hmal^-$ (1880 M^{-1} s^{-1} [1]) is but slightly higher than that of $Co(Hmal)^{2+}$, indicating the minor importance of electrostatic factors. Free mal^{2-} is much more reactive (1000 M^{-1} s^{-1} [1]) than $Co(mal)^+$, in full contrast to what could be expected on electrostatic grounds. The behaviour of $Co(mal)^+$ cannot be explained by steric effects either since these should be operative also with $Co(Hmal)^{2+}$, which however is not the case.

The low reactivity of $Co(mal)^+$ can be ascribed to a conjugative shift of electron density from the uncoordinated carboxylate group towards the cobalt(III) center, which would make the near-concerted nucleophilic attack of MnO_4^- on the double bond more difficult. In $Co(Hmal)^{2+}$ this shift is less pronounced, being counterbalanced by the proton in the carboxy group. This behaviour is in line with earlier results on the relative reactivities of maleic acid derivatives and lends additional support to the view that olefin oxidation by MnO_4^- involves nucleophilic attack on the double bond [1, 2].

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