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Kinetics and Mechanisms of the Oxidation by Permanganate of L-Alanine

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The oxidation of L-alanine by permanganate ion in aqueous phosphate buffers is autocatalysed by the inorganic reaction product, a soluble form of colloidal manganese dioxide temporarily stabilized in solution by adsorption of phosphate ion on its surface. The rate of the non-catalytic reaction pathway is first-order in both the oxidizing and reducing agent, is not affected by potassium chloride addition to the solution, and increases with the pH of the medium, its associated activation energy being 74.0 kJ mol^{-1}. The rate of the catalytic reaction pathway is first order in both the oxidizing and autocatalytic agent, follows the Freundlich adsorption isotherm as far as the reducing agent concentration is concerned, is not affected by potassium chloride addition to the solution, and increases with the pH of the medium, its associated activation energy being 67.2 kJ mol^{-1}. Mechanisms consistent with the experimental data are proposed.

The kinetic and mechanistic study of the oxidation of amino acids is of interest because of its biological importance. However, this topic has not received much attention, save for a few kinetic studies.[1-4] The present paper deals with the reaction between L-alanine and permanganate ion in neutral aqueous solution. This reaction shows the behaviour of a typical autocatalytic process. Owing to the fact that the information available on the kinetic and mechanistic aspects of autocatalytic reactions is rather scarce, special care has been put into obtaining reliable kinetic data for this reaction.

Experimental

The solvent was water twice distilled in an all-glass apparatus. The oxidizing agent was potassium permanganate (Merck) and the reducing agent L-alanine (Scharlau). A KH_2PO_4–K_2HPO_4 (both Merck) buffer was used to keep the pH of the medium constant and prevent manganese dioxide from precipitating while the reaction was being monitored. Potassium chloride (Panreac) was used to modify the ionic strength of the medium.

Permanganate ion was chosen as the rate-monitoring species. The disappearance of permanganate was followed with a thermostatted Varian Cary 219 spectrophotometer. The pH was determined by a Präzisions pH-Meter E510 provided with a combined electrode and calibrated with commercial buffers.

Results

Figure 1 shows that the inorganic product absorbs radiation in the visible region. The band shows a rather shapeless pattern, so that when the logarithm of the absorbance is plotted against the logarithm of the wavelength a linear correlation is achieved (slope −5.25). The colour of the solutions at the end of reaction was dark yellow; although turbidity was never observed a brown precipitate was always observed one day after reaction.

As the inorganic product absorbs light in the whole visible spectrum, it is necessary to correct the absorbances to obtain the permanganate concentration from the absorbance both at 418 (where only the product absorbs light) and at 526 nm (where both reactant and product absorb light). The permanganate concentration is then obtained by equation

$$c = (A^{526} - \varepsilon_P^{526} A^{418}/\varepsilon_P^{418})/\varepsilon_R^{526} \qquad (1)$$

(1) where the subscripts R and P stand for reactant and product, respectively.[5] The extinction coefficient of the reactant at 526 nm is ε_R^{526} 2.40 × 10^3 mol^{-1} dm^3 cm^{-1},[6] and the extinction coefficients of the product at 418 and 526 nm (ε_P^{418} and ε_P^{526}) can be derived from the final absorbance readings.

The initial-rate method was used to determine the kinetic order of the reaction with respect to permanganate ion; as Table 1 shows, the initial rates are directly proportional to the initial permanganate concentration, *i.e.*, the kinetic order

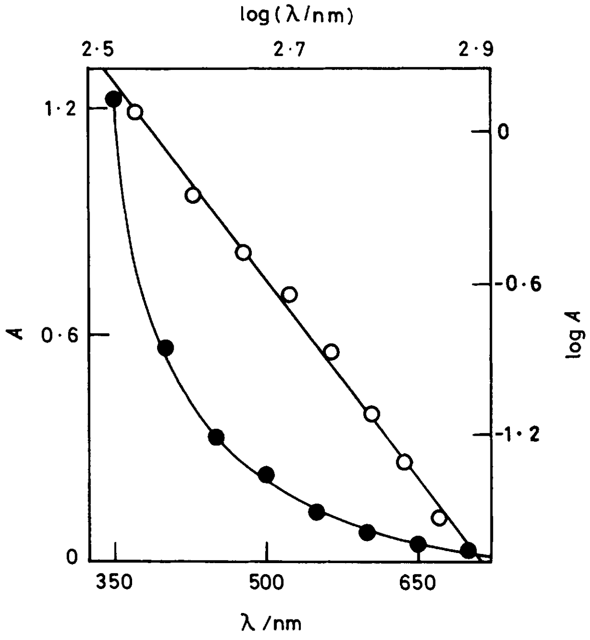

Figure 1. Visible spectrum and log *A versus* log λ linear plot for the inorganic reaction product. [MnO_4^-] 5 × 10^{-4} mol dm^{-3}; [alanine] 0.05 mol dm^{-3}; pH 7.59; temperature 25.0 °C. Correlation coefficient of the linear plot 0.997

Table 1. Initial rate constants at several permanganate concentrations. [alanine] 0.05 mol dm^{-3}; pH 7.59; temperature 45.0 °C

10^4c_0/mol dm^{-3}	5.98	6.79	7.86	8.94	10.01
10^7r_0/mol dm^{-3} s^{-1}	1.32	1.54	1.77	2.07	2.20
$10^4(r_0/c_0)$/s^{-1}	2.21	2.27	2.25	2.32	2.20

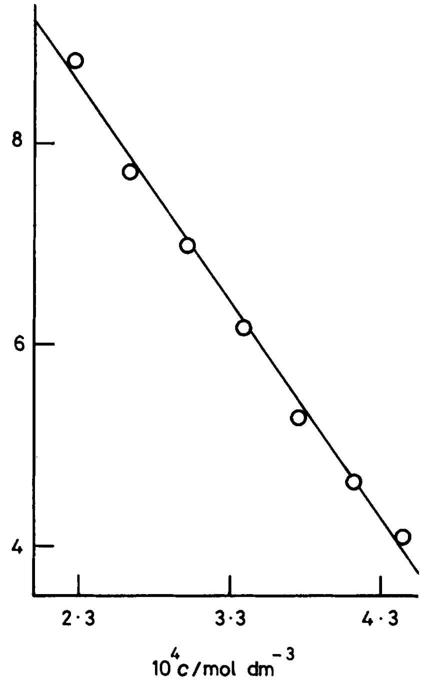

Figure 2. r/c *versus* c plot for the oxidation of alanine (0.05 mol dm^{-3}) by permanganate ion (5×10^{-4} mol dm^{-3}) at pH 7.59 and 25.0 °C. Linear correlation coefficient 0.996

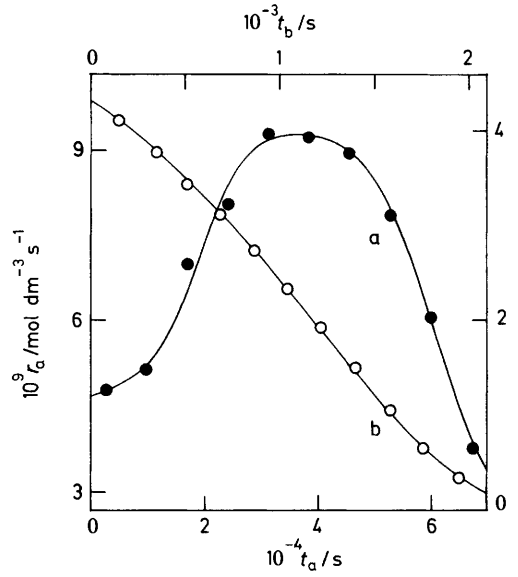

Figure 3. Reaction rate *versus* time plots: a, [MnO_4^-] 5×10^{-4} mol dm^{-3}; [alanine] 0.07 mol dm^{-3}; pH 6.49; temperature 25.0 °C; b, [MnO_4^-] 5×10^{-4} mol dm^{-3}; [alanine] 0.26 mol dm^{-3}; pH 8.25; temperature 25.0 °C

in permanganate ion is unity. Thus, when the ratio between the reaction rate and the permanganate concentration was plotted against the latter, a horizontal straight line was expected to be found, in contrast to the situation evident in Figure 2 for a typical experiment. Moreover, when the reaction rate is plotted against time either a bell-shaped curve (Figure 3a) or a continuously decreasing one (Figure 3b) is obtained depending on the experimental conditions. Bell-shaped plots similar to that in Figure 3a have been reported for the permanganate oxidation of compounds closely related to amino acids, *e.g.* aliphatic amines.[7–9]

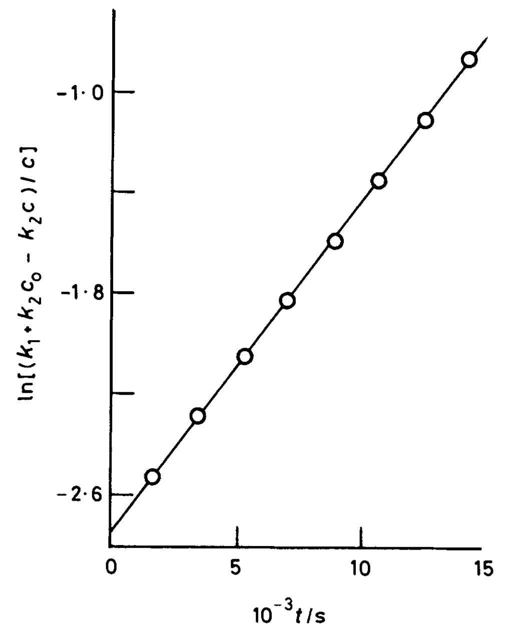

Figure 4. Rate-law plot for the oxidation of alanine (0.05 mol dm^{-3}) by permanganate ion (5×10^{-4} mol dm^{-3}) at pH 7.59 and 25.0 °C. Linear correlation coefficient 0.999 97

These results show that the reaction is autocatalytic. Hence, at least two mechanisms are involved, one being responsible for initial product formation and the other using the autocatalytic product. Since alanine was present in great excess with respect to permanganate, the simplest differential rate law is given by equation (2) where c and c_0 are the permanganate concentrations at time t and 0 so that $(c_0 - c)$ is the autocatalytic product concentration provided that one mole of permanganate gives one mole of autocatalytic product. If some other stoicheiometric relation holds, the autocatalytic product concentration will be directly proportional to $(c_0 - c)$ and the mathematic form of the differential rate law will still be valid. In equation (2) k_1 and k_2 are the pseudo-rate constants of the non-catalytic and catalytic pathways, respectively.

$$-\mathrm{d}c/\mathrm{d}t = k_1c + k_2c(c_0 - c) \qquad (2)$$

Equation (2) is in full agreement with the kind of relationship shown in Figure 2, for it can also be written in the form (3) where

$$r/c = (k_1 + k_2c_0) - k_2c \qquad (3)$$

r is the reaction rate ($r = -\mathrm{d}c/\mathrm{d}t$). So, when r/c is plotted against c a straight line with a negative slope is obtained (see Figure 2).

By applying equation (3) to the results of the different kinetic runs the k_1 and k_2 values can be derived. In addition, more accurate values of the rate constants can be obtained if an integral rate law is used; by integration of equation (2) we can obtain equation (4). The values of k_1 and k_2 can be derived by

$$\ln[(k_1 + k_2c_0 - k_2c)/c] = \ln(k_1/c_0) + (k_1 + k_2c_0)t \qquad (4)$$

using equation (4) in an iterative way. A plot of the left-hand side of equation (4) against time then yields a straight line (see Figure 4). Equation (4) gives good linear correlation coefficients (0.9992—0.999 98) in all experiments.

We can conclude that equation (2) also applies; hence, the kinetic order of permanganate ion in both non-catalytic and

Table 2. Rate constants at several potassium chloride concentrations. $[\mathrm{MnO_4^-}]$ 5×10^{-4} mol dm^{-3}; [alanine] 0.05 mol dm^{-3}; pH 7.59; temperature 25.0 °C

$[\mathrm{KCl}]$/mol dm^{-3}	0.00	0.12	0.24	0.36	0.48
10^5k_1/s^{-1}	2.98	3.16	3.01	3.01	2.99
k_2/mol^{-1} dm^3 s^{-1}	0.213	0.203	0.208	0.203	0.195

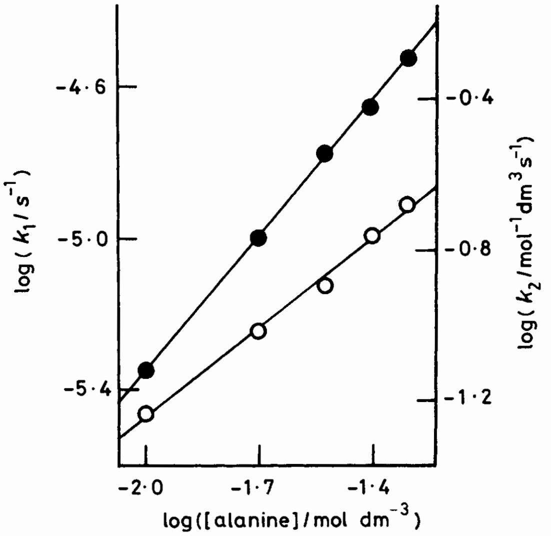

Figure 5. Dependence of the rate constants on the alanine concentration: $[\mathrm{MnO_4^-}]$ 5×10^{-4} mol dm^{-3}; pH 7.59; temperature 25.0 °C. Linear correlation coefficients 0.9997 (k_1, solid circles) and 0.997 (k_2, open circles)

catalytic pathways, as well as that of the autocatalytic product in the catalytic pathway, is always unity. As far as the non-catalytic pathway is concerned, this information is consistent with the experimental data in Table 1.

Figure 5 shows that the logarithms of both k_1 and k_2 are linear when plotted against the log [alanine]; the respective slopes are 1.17 and 0.79. On the other hand, no salt effect was found (see Table 2). Figure 6 shows that both log k_1 and log k_2 increase linearly with pH (respective slopes 0.75 and 0.39). Finally, Figure 7 shows that both k_1 and k_2 obey the Arrhenius equation (activation energies 74.0 and 67.2 kJ mol^{-1}, respectively).

Discussion

As pH range (6.08—7.59) was close to the isoelectric point of alanine (6.11), the zwitterionic form of the amino acid was dominant. For the non-catalytic pathway, oxidation by permanganate might occur by equations (5)—(10).

$$\mathrm{CH_3CH(\overset{+}{N}H_3)CO_2^- + MnO_4^- \xrightarrow{slow} CH_3CH(\overset{+}{N}H_3)CO_2^{\bullet} + MnO_4^{2-}} \quad (5)$$

$$\mathrm{CH_3CH(\overset{+}{N}H_3)CO_2^{\bullet} \longrightarrow CH_3\dot{C}H\overset{+}{N}H_3 + CO_2} \quad (6)$$

$$\mathrm{CH_3\dot{C}H\overset{+}{N}H_3 \longrightarrow CH_3\dot{C}HNH_2 + H^+} \quad (7)$$

$$\mathrm{CH_3\dot{C}HNH_2 + MnO_4^- \longrightarrow CH_3CH{=}\overset{+}{N}H_2 + MnO_4^{2-}} \quad (8)$$

$$\mathrm{CH_3CH{=}\overset{+}{N}H_2 + H_2O \longrightarrow CH_3CHO + NH_4^+} \quad (9)$$

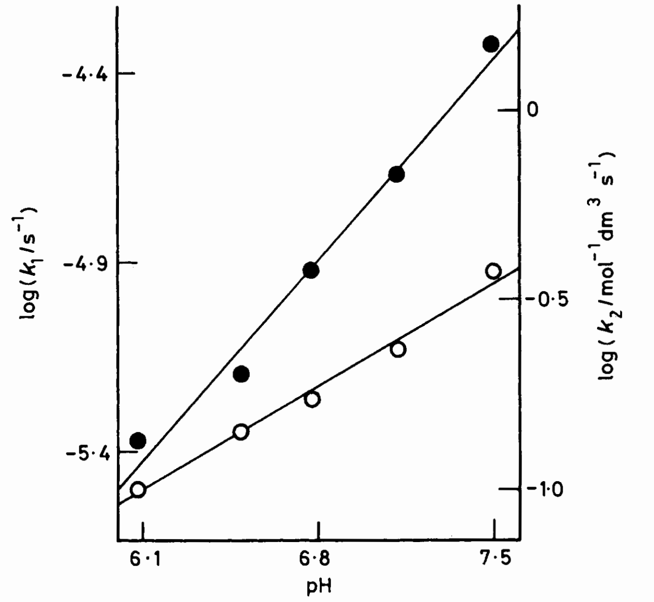

Figure 6. Dependence of the rate constants on the pH: $[\mathrm{MnO_4^-}]$ 5×10^{-4} mol dm^{-3}; [alanine] 0.07 mol dm^{-3}; temperature 25.0 °C. Linear correlation coefficients 0.991 (k_1, solid circles) and 0.993 (k_2, open circles)

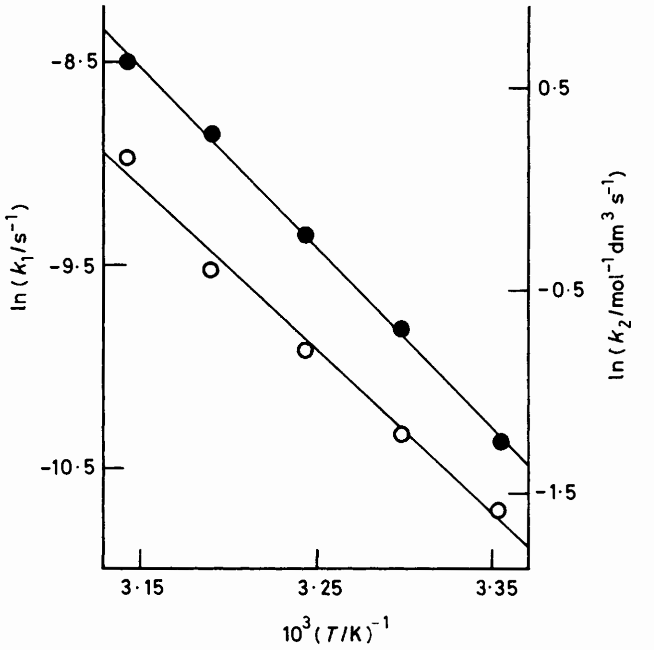

Figure 7. Arrhenius plots: $[\mathrm{MnO_4^-}]$ 5×10^{-4} mol dm^{-3}; [alanine] 0.05 mol dm^{-3}; pH 7.59. Linear correlation coefficients 0.999 (k_1, solid circles) and 0.994 (k_2, open circles)

$$\mathrm{3\,MnO_4^{2-} + 2\,H_2O \longrightarrow 2\,MnO_4^- + MnO_2 + 4\,OH^-} \quad (10)$$

In equation (5), one-electron transfer from the organic substrate to permanganate ion results in the formation of manganate ion and a cation radical. The latter gives another cation radical by decarboxylation, as depicted in equation (6). Deprotonation of the second cation radical yields a neutral free radical in equation (7), this step being similar to that proposed for the permanganate oxidation of trimethylamine.[10] Oxidation of the neutral free radical by permanganate ion in equation (8) gives ethyliminium ion (imines are known to be intermediate species in the permanganate oxidation of amines[11]). Hydrolysis of ethyliminium ion results in acetaldehyde and ammonium ion formation [equation (9)]. Finally, by dismutation of manganate ion the permanganate ion consumed in equations (5) and (8) is partially reformed while manganese dioxide is obtained as the inorganic product of the reaction, equation (10) being extremely fast in all but very alkaline media.[12]

It has been reported that carbon dioxide,[13] aldehydes,[14] and ammonia[15] are all obtained by permanganate oxidation of amino acids. A brown precipitate of managanese dioxide was detected one day after completion of the reaction. These findings are in full agreement with the proposed mechanism.

Although equations (5)—(10) make an important contribution to the non-catalytic pathway, Figure 6 indicates that an increase in the pH results in an increase in the rate constant of the non-catalytic pathway; this cannot be interpreted exclusively in terms of equations (5)—(10) and, therefore, oxidation of the anionic form of the amino acid must also take place [equations (11) and (12)]. Once $CH_3\dot{C}HNH_2$ is formed, its disappearance will follow equations (8) and (9).

$$CH_3CH(NH_2)CO_2^- + MnO_4^- \xrightarrow{\text{slow}} CH_3CH(NH_2)CO_2^{\cdot} + MnO_4^{2-} \quad (11)$$

$$CH_3CH(NH_2)CO_2^{\cdot} \longrightarrow CH_3\dot{C}HNH_2 + CO_2 \quad (12)$$

With respect to the possible oxidation of the cationic form of the amino acid, although permanganate oxidation of amino acids in concentrated acidic media was postulated to happen by reaction between the cationic form of the amino acid and permanganic acid,[2] the concentrations of those two species in neutral solutions are certainly too small to react with each other at a measurable rate.

The velocity of permanganate consumption through the non-catalytic pathway is given by the two rate-determining steps, equations (5) and (11), as indicated by equation (13) where r_1 is

$$r_1 = k_5[MnO_4^-][HA] + k_{11}[MnO_4^-][A^-] \quad (13)$$

the rate of the non-catalytic pathway, k_5 and k_{11} stand for the rate constants for equations (5) and (11), and [HA] and $[A^-]$ represent the concentrations of the zwitterionic and anionic forms of the amino acid, respectively.

As [HA] and $[A^-]$ are directly proportional to the total alanine concentration [equations (14) and (15)], K_1 and K_2

$$[HA] = [\text{alanine}][H^+]/(K_2 + [H^+] + [H^+]^2/K_1) \quad (14)$$

$$[A^-] = [\text{alanine}]/(1 + [H^+]/K_2 + [H^+]^2/K_1K_2) \quad (15)$$

being the dissociation constants of the cationic (H_2A^+) and zwitterionic (HA) forms of the amino acid, respectively, we can conclude from equation (13) that the non-catalytic reaction pathway is first order in both permanganate ion and L-alanine (Table 1 and Figure 5).

The rate constant of the non-catalytic reaction pathway is given by the ratio between r_1 and $[MnO_4^-]$; from equation (13) the expression obtained for k_1 is (16).

$$k_1 = k_5[HA] + k_{11}[A^-] \quad (16)$$

From equations (14) and (15) the concentrations of the zwitterionic and anionic forms of the amino acid were derived and compiled in Table 3 along with the k_1 values. Owing to the closeness of the pH range to the isoelectric point of alanine, [HA] is practically constant; hence, from equation (16), the relationship between k_1 and $[A^-]$ is linear. Application of the least-squares method to the k_1 and $[A^-]$ values in Table 3 yields equation (17), the associated linear correlation coefficient being

Table 3. Rate constants of the non-catalytic pathway at several pH values and respective contributions from the zwitterionic and anionic forms of the amino acid. $[MnO_4^-]$ 5 × 10^{-4} mol dm^{-3}; [alanine] 0.07 mol dm^{-3}; temperature 25.0 °C

pH	6.08	6.49	6.79	7.12	7.50
10^2[HA]/mol dm^{-3}	7.00	7.00	6.99	6.99	6.97
$10^4[A^-]$/mol dm^{-3}	0.11	0.29	0.59	1.25	3.00
$10^5(k_5[HA] + k_{11}[A^-])/s^{-1}$	0.42	0.69	1.14	2.13	4.75
$10^5k_1/s^{-1}$	0.43	0.63	1.20	2.15	4.74

$$k_1 = 2.55 \times 10^{-6} + 0.150[A^-] \quad (17)$$

0.9996. Therefore, if [HA] 6.99 × 10^{-2} mol dm^{-3} is taken as an average value for the concentration of the zwitterion, comparison between equations (16) and (17) allows k_5 and k_{11} to be estimated. The values obtained are k_5 3.65 × 10^{-5} mol^{-1} dm^3 s^{-1} and k_{11} 0.150 mol^{-1} dm^3 s^{-1}. Table 3 shows that the value of $(k_5[HA] + k_{11}[A^-])$ approaches that of the experimental k_1 at every pH.

We can see that the rate constant for the reaction between the anionic form of the amino acid and permanganate ion is much larger than that corresponding to the zwitterionic form. It can be inferred that the increase in the electron density of the anion compared with that of the zwitterion, which results in an increase in the reducing power of the former, easily overcomes the unfavourable effect of electrostatic repulsion between the anion of the amino acid and permanganate ion.

For the ionic strength, it is evident from the results in Table 2 that salt effects on k_5 and k_{11} [see equation (16)] and on K_1 and K_2 [see equations (14) and (15)] are somehow compensated. It is also interesting to note that the activation energy found for the non-catalytic reaction pathway (74.0 kJ mol^{-1}) is only an apparent value, since the effects of temperature on k_5, k_{11}, K_1, and K_2 are all included in the experimental activation energy.

For the catalytic pathway, the autocatalytic product must be identified. Figure 1 suggests that the visible spectrum of the inorganic product might be due to scattering rather than absorption of light, although the slope of the log A–log λ linear plot indicates a slight deviation of the experimental value (−5.25) from the theoretical one (−4) predicted by Rayleigh's law. Thus, it can be concluded that the nature of the manganese product is colloidal. A soluble form of colloidal manganese dioxide temporarily stabilized in solution by adsorption of phosphate ion on its surface has been identified in many permanganate reactions performed in aqueous phosphate buffer.[16–18] When quaternary ammonium permanganate is reduced by organic substrates in methylene dichloride, a soluble form of colloidal manganese dioxide stabilized in solution by adsorption of the excess of organic substrate on its surface has been identified.[19] It is interesting that the spectra reported for the manganese products from all these reactions are similar to ours.

Furthermore, it has been pointed out that colloidal manganese dioxide is responsible for the autocatalysis observed in many permanganate reactions.[5,7–9,20,21] Thus, it seems reasonable to assume that the soluble form of colloidal manganese dioxide is the autocatalytic agent here.

According to this criterion, the mechanism for the catalytic pathway is given in equations (18) and (19)

$$MnO_2 + CH_3CH(\overset{+}{N}H_3)CO_2^- \rightleftharpoons \text{Adsorbate} \quad (18)$$

$$\text{Adsorbate} + MnO_4^- \xrightarrow{\text{slow}} \text{Products} \quad (19)$$

First, the zwitterion of the amino acid (predominant in the pH range) is adsorbed on the surface of colloidal manganese dioxide [see equation (18)]. The adsorbed species is then oxidized by permanganate ion from the solution surrounding the colloidal particles [equation (19)].

The rate law associated with this mechanism is (20) where r_2

$$r_2 = k_{19}[\mathrm{MnO_4}^-][\text{adsorbate}] \tag{20}$$

is the rate corresponding to the catalytic pathway and k_{19} is the rate constant for equation (19).

If equilibrium (18) is very fast compared with (19), the adsorbate concentration will be given by an adsorption isotherm, for instance, the Freundlich isotherm;[22] therefore, the ratio between the adsorbate and colloid concentrations is given by equation (21) and from equations (20) and (21) we obtain (22).

$$[\text{adsorbate}]/[\mathrm{MnO_2}] = a[\text{alanine}]^b \tag{21}$$

$$r_2 = k_{19}a[\mathrm{MnO_4}][\mathrm{MnO_2}][\text{alanine}]^b \tag{22}$$

Thus, the catalytic pathway is first order in both the electrophilic ($\mathrm{MnO_4}^-$) and autocatalytic ($\mathrm{MnO_2}$) agents, in full agreement with the differential rate law which was experimentally confirmed [see equation (2) and Figures 2 and 4].

On the other hand, comparison between equations (2) and (22) leads to equation (23), in full agreement with the

$$k_2 = k_{19}a[\text{alanine}]^b \tag{23}$$

experimental findings, for the log k_2–log [alanine] plot is linear (see Figure 5). Furthermore, its slope is fractional (b 0.79) as required by the Freundlich isotherm.

It has been found that log k_2 increases linearly as the pH of the solution increases (see Figure 6), the corresponding slope being 0.39; this agrees qualitatively and quantitatively with the situation found for adsorption of many substrates on the surface of colloidal manganese dioxide, for which hydroxide ions linked to manganese dioxide play an important role as active sites at the colloid surface.[23–25]

As Table 2 reveals, the ionic strength of the medium does not significantly affect the k_2 value (there is, a very minor decrease in k_2 as the potassium chloride concentration increases). According to equation (23) the salt effects on k_{19} and on the Freundlich parameters a and b must be roughly compensated. For the dependence of k_2 on temperature, the activation energy for the catalytic pathway (67.2 kJ mol^{-1}) is an apparent value, as for the non-catalytic pathway, as the dependence of k_{19} and the Freundlich parameters on temperature is included.

Finally, it is noteworthy that the reaction rate–time plots are sometimes bell-shaped and sometimes uniformly decreasing depending on the experimental conditions (see Figure 3). Although at first impression it may be concluded that there are two different kinetic situations, with and without autocatalysis, the use of the differential rate law leads to another conclusion.

From equation (2) we obtain (24) where r_2/r is the ratio

$$r_2/r = k_2(c_0 - c)/[k_1 + k_2(c_0 - c)] \tag{24}$$

between the rate of the catalytic pathway and the total reaction rate. Moreover, from equation (4) the permanganate concentration can be expressed as the function of time of equation (25). According to equations (24) and (25) we can see

$$c = (k_1 + k_2c_0)/[k_2 + (k_1/c_0)\exp(k_1 + k_2c_0)t] \tag{25}$$

that r_2/r varies within the limits given by equations (26) and (27).

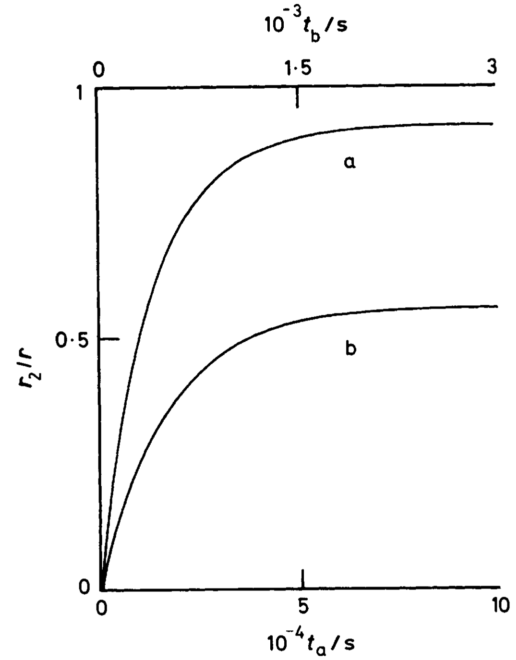

Figure 8. r_2/r *versus* time plots: a, [$\mathrm{MnO_4}^-$] 5 × 10^{-4} mol dm^{-3}; [alanine] 0.07 mol dm^{-3}; pH 6.49; temperature 25.0 °C; b, [$\mathrm{MnO_4}^-$] 5 × 10^{-4} mol dm^{-3}; [alanine] 0.26 mol dm^{-3}; pH 8.25; temperature 25.0 °C

$$\lim_{t\to 0}(r_2/r) = 0 \tag{26}$$

$$\lim_{t\to \infty}(r_2/r) = k_2c_0/(k_1 + k_2c_0) \tag{27}$$

Thus, r_2/r can be plotted against time, as we have done in Figure 8 for the same experiments on which Figure 3 was based. We can see that the superior limit for r_2/r takes the values 0.92 (Figure 8a) and 0.56 (Figure 8b). If equation (27) represents a measure of the proportion of catalytic pathway with respect to the total reaction, we can conclude that reduction of the bell-shaped profile of Figure 3b compared with that of Figure 3a is a consequence of a decrease in the relative importance of the contribution due to the catalytic reaction pathway. It does not mean disappearance of the autocatalytic phenomenon. Therefore, there must be a certain value of the limit given by equation (27) at which the reaction rate–time curves lose their characteristic bell-shaped pattern, although only a zero value for that limit would indicate that the reaction is not autocatalytic.

Acknowledgements

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